

Esa Saukkonen

**EFFECTS OF THE PARTIAL REMOVAL OF WOOD
HEMICELLULOSES ON THE PROPERTIES OF
KRAFT PULP**

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in Auditorium 1383 at Lappeenranta University of Technology, Lappeenranta, Finland on the 4th of December, 2014, at noon.

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ABSTRACT

Esa Saukkonen

Effects of the partial removal of wood hemicelluloses on the properties of kraft pulp

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The objective of this work was to study the effects of partial removal of wood hemicelluloses on the properties of kraft pulp. The work was conducted by extracting hemicelluloses (1) by a softwood chip pretreatment process prior to kraft pulping, (2) by alkaline extraction from bleached birch kraft pulp, and (3) by enzymatic treatment, xylanase treatment in particular, of bleached birch kraft pulp. The qualitative and quantitative changes in fibers and paper properties were evaluated. In addition, the applicability of the extraction concepts and hemicellulose-extracted birch kraft pulp as a raw material in papermaking was evaluated in a pilot-scale papermaking environment. The results showed that each examined hemicellulose extraction method has its characteristic effects on fiber properties, seen as differences in both the physical and chemical nature of the fibers.

A prehydrolysis process prior to the kraft pulping process offered reductions in cooking time, bleaching chemical consumption and produced fibers with low hemicellulose content that are more susceptible to mechanically induced damages and dislocations. Softwood chip pretreatment for hemicellulose recovery prior to cooking, whether acidic or alkaline, had an impact on the physical properties of the non-refined and refined pulp. In addition, all the pretreated pulps exhibited slower beating response than the unhydrolyzed reference pulp. Both alkaline extraction and enzymatic (xylanase) treatment of bleached birch kraft pulp fibers indicated very selective hemicellulose removal, particularly xylan removal. Furthermore, these two hemicellulose-extracted birch kraft pulps were utilized in a pilot-scale papermaking environment in order to evaluate the upscalability of the extraction concepts. Investigations made using pilot paper machine trials revealed that some amount of alkaline-extracted birch kraft pulp, with a 24.9% reduction in the total amount of xylan, could be used in the papermaking stock as a mixture with non-extracted pulp when producing 75 g/m² paper. For xylanase-treated fibers there were no reductions in the mechanical properties of the 180 g/m² paper produced compared to paper made from the control pulp, although there was a 14.2% reduction in the total amount of xylan in the xylanase-treated pulp compared to the control birch kraft pulp.

This work emphasized the importance of the hemicellulose extraction method in providing new solutions to create functional fibers and in providing a valuable hemicellulose co-product stream. The hemicellulose removal concept therefore plays an important role in the integrated forest biorefinery scenario, where the target is to the co-production of hemicellulose-extracted pulp and hemicellulose-based chemicals or fuels.

Keywords: alkaline extraction, forest biorefining, hemicelluloses, prehydrolysis-kraft pulp, xylan, xylanase treatment

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Lappeenranta, October 2014

Esa Saukkonen

LIST OF PUBLICATIONS

The thesis is based on the original publications listed below, which are referred to in the text by their Roman numerals, and additional previously unpublished experimental work.

- I Kautto, J., Saukkonen, E. and Henricson, K. (2010) Digestibility and paper-making properties of prehydrolyzed softwood chips, *BioResources*, 5(4):2502–2519
- II Saukkonen, E., Kautto, J., Rauvanto, I. and Backfolk, K. (2012) Characteristics of prehydrolysis-kraft pulp fibers from Scots pine, *Holzforschung*, 66(7):801–808
- III Saukkonen, E., Lyytikäinen, K. and Backfolk, K. (2012) Alkaline xylan extraction of bleached kraft pulp - effect of extraction time on pulp chemical composition and physical properties, *Tappi Journal*, 11(4):37–43
- IV Saukkonen, E., Lyytikäinen, K., Geydt, P. and Backfolk, K. (2014) Surface selective removal of xylan from refined never-dried birch kraft pulp, *Cellulose*, 21(5):3677–3690

AUTHOR'S CONTRIBUTION TO THE WORK PRESENTED IN THE LISTED PUBLICATIONS

All publications are a result of work with the supervisors, co-authors and other research partners in both the Future Biorefinery (FuBio) program of Finnish Bioeconomy Cluster, FIBIC Ltd (former ForestCluster Ltd), and the Biorefinery Pulp Mill (BiSe) project funded by TEKES and industrial partners.

- I Responsible author on the effects of prehydrolysis on pulp bleachability and fiber properties. Interpretation of the results, writing the manuscript with Jesse Kautto (M.Sc. Tech.).

- II Planning the experimental setup for wood chip prehydrolysis and cooking together with Jesse Kautto (M.Sc. Tech.). Coordinating the pulp bleaching and pulp and paper properties testing. Interpretation of the results and writing the manuscript.
- III Planning of trials together with Katja Lyytikäinen (M.Sc. Tech.), pulp and paper testing, and interpretation of the results. Writing the majority of the manuscript.
- IV Planning of the xylanase treatment trials and experimental setup for pulp and paper testing. Pulp and paper testing together with laboratory assistants. Interpretation of the results and writing the manuscript.

SUPPORTING PUBLICATIONS

1. Lyytikäinen, K., Saukkonen, E., Kajanto, I., Käyhkö, J. (2011) The effect of hemicellulose extraction on fiber charge properties and retention behavior of kraft pulp fibers, *BioResources*, 6(1):219–231
2. Stepanov, A., Piili H., Saukkonen, E. and Salminen, A. (2011) Effect of Linear Cutting Energy on Coloration of Paper in Laser Cutting of Paper Material, Oral presentation, 30th International Congress on Applications of Lasers & Electro-Optics ICALEO, 23–27 October 2011, Orlando, FL, USA, 71–79
3. Tanninen, P., Lindell, H., Saukkonen, E. and Backfolk, K. (2013) Thermal and mechanical durability of starch-based dual polymer barrier coatings in the press forming of paperboard, *Packaging Technology and Science*, 27(5):353–363
4. Lyytikäinen, K., Saukkonen, E., Väisänen, M., Timonen, J. and Backfolk, K. (2014) Effect of reduced pulp xylan content on wet end chemistry and paper properties - A pilot scale study, *Tappi Journal*, 13(2):29–37
5. Ovaska, S-S., Mielonen, K., Saukkonen, E., Lozovski, T., Rinkunas, R., Sidaravicius, J. and Backfolk, K. (2014) A Novel Method to Study the Effect of Corona Treatment on Ink Wetting and Sorption Behavior, NIP30 and Digital fabrication, Society for Imaging Science and Technology, 7–11 September 2014, Philadelphia, PA, USA, 362–365

ABBREVIATIONS

Ac	Acetyl
AcidH	Dilute-acid prehydrolysis
AFM	Atomic force microscopy
AG	Arabinogalactan
AGX	Arabinoglucuronoxylan
AlkE	Alkaline extraction
AOX	Adsorbable organic halogens
AQ	Anthraquinone
Ara	Arabinose
BBKP	Bleached birch kraft pulp
CD	Cross direction
ClO ₂	Chlorine dioxide
COD	Chemical oxygen demand
CSA	Cross-sectional area
CSF	Canadian standard freeness
CWT	Cell wall thickness
DED	Chlorine dioxide – Sodium Hydroxide – Chlorine Dioxide
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
EA	Effective alkali
ECF	Elementary chlorine free
FSP	Fiber saturation point
Gal	Galactose
GalpA	Galacturonic acid
GGM	Galactoglucomannan
Glc	Glucose
Glc pA	Glucuronic acid
GM	Glucomannan
GX	Glucuronoxylan
H ₂ SO ₄	Sulfuric acid

HW	Hardwood
IFBR	Integrated forest biorefinery
ISO	International Standards Organization
kWh	Kilowatt-hour
LSC	Light-scattering coefficient
M	Molar
Man	Mannose
MFA	Microfibril angle
MD	Machine direction
Me	Methyl
NaBH ₄	Sodium borohydride
NaOH	Sodium hydroxide
nkat	Nanokatal
odw	Oven dry wood
P	Primary cell wall
PFI	Paper and Fibre Research Institute
PHW	Pressurized hot-water extraction
PM	Papermaking
PPS	Parker print surf
PS	Polysulfide
R pulp	Reference pulp
Ref	Reference
Rha	Rhamnose
RI	Reinforcement index
S ₁₋₃	Secondary cell wall layers
SCAN	Scandinavian Pulp, Paper and Board
SEC	Specific energy consumption
SEL	Specific edge load
SEM	Scanning electron microscopy
SR	Schopper-Riegler
SW	Softwood
TEA	Tensile energy adsorption

TOC	Total organic carbon
TSI	Tensile stiffness index
VPP	Value prior to pulping
WRV	Water retention value
WZST	Wet zero-span tensile strength
XGR	Xylan-to-glucose ratio
XO	Xylooligosaccharide
XT	Xylanase-treated
Xyl	Xylose

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1 INTRODUCTION

1.1 Background

The pulp and paper industry has the reputation of being a relatively conservative, path-dependent and mature industry and has been characterized by large consolidations based on economies of scale, where competitive advantage is achieved by decreasing average total costs due to improved technological or organizational efficiency (Toivanen 2004). However, the hunt for cost savings can drive companies to a situation where further developments are no longer worthwhile (Peltoniemi 2013). Consequently, many companies in the pulp and paper industry, especially in mature markets, are struggling with declining profits and challenges within the external operational environment. Therefore, these companies could benefit from reconsidering their current production concepts. The mentality of “tonnes of product per day”, i.e., the ‘*economies of scale*’ production focus, will have to be changed through market demand and product value, i.e., to focusing more on ‘*economies of scope*’ and/or niches. Therefore, one alternative for increasing the value creation potential for integrated pulp and paper mills might be to develop sustainable competitive advantage from forest biorefining operations (van Heiningen 2006; Pätäri et al. 2011). The transformation of a traditional pulp mill into an integrated forest biorefinery (IFBR) efficiently utilizing all the wood-derived biomass brought to the mill presents a promising opportunity for enterprise revival of the pulp and paper industry by maintaining the profitability of the old business functions, whilst offering new sources of revenue from various biorefining operations (Christopher 2012).

An IFBR builds on the same principles as the petrochemical refinery: “use every drop”. In a petrochemical refinery, the raw material is normally crude oil, whereas in a forest biorefinery the raw material would be wood, other biomass, or process residues. The purpose of an IFBR approach is to maximize the value of as many fractions of the wood material as possible by producing economically viable biorefinery products. Thereby, IFBRs have a great potential for economic production of biofuels, biochemicals, and biomaterials in addition to traditional pulp, paper, and wood products. Figure 1 depicts an envisioned transformation of a traditional pulp mill into an advanced biorefinery utilizing the wood-derived biomass thoroughly.

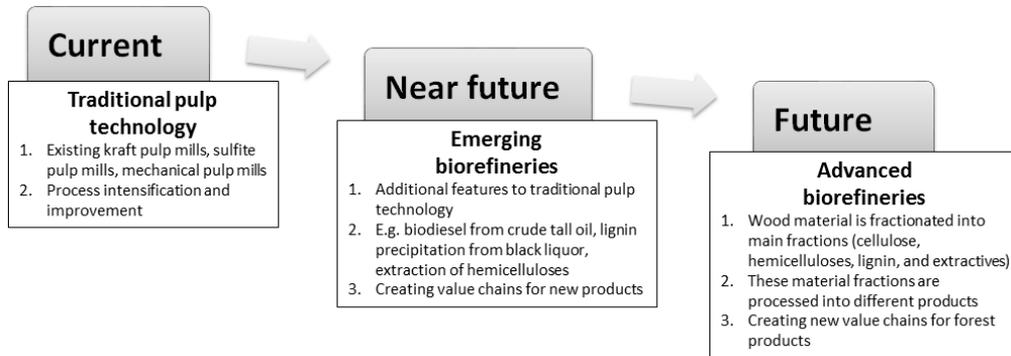


Figure 1 Transformation of current traditional pulp technology into an emerging/advanced biorefinery.

There are a large variety of chemicals that could be extracted or recovered from forest resources and processed into bio-based products (Kamm and Kamm 2004). However, there is a difference between products that should be produced in an IFBR and which products could be produced in a sustainable and economical manner. Therefore, each mill needs to define its own “best choice” products, based, for example, on market pull and the mill potential to target this market. This means that pulp mills can add new process alternatives and evolve into forest biorefineries by whatever path is most attractive to them. Thus, the IFBR concept offers new sources of revenue and can result in significantly improved profitability, if optimized and tailored to the individual mill. In the transitional period from traditional pulp mills to emerging or advanced biorefineries, the mills could benefit from process alternatives that can be integrated with existing unit operations. Consequently, a large number of potential forest biorefinery processes for existing pulp mills have recently been proposed (Zhang et al. 2011a). One such process step for a traditional pulp mill would be the extraction of hemicelluloses, allowing co-production of hemicellulose-extracted pulp and hemicellulose-based chemicals or fuels.

Despite the attention in academia paid to hemicellulose extraction, the utilization possibilities for the extracted hemicelluloses, and the effect of the hemicellulose content on fiber and paper properties, remarkably little research has focused on the alternative hemicellulose extraction processes and their distinct effects on the properties of paper-grade pulp fibers. Thereby, the motivation for this work was to focus on the various hemicellulose extraction processes for partial removal of hemicelluloses from wood and pulp material. In particular, the effect of the partial removal of wood hemicelluloses on fiber characteristics and paper properties of kraft

pulp is discussed. This knowledge is needed in order to find the most advantageous process concepts for different forest biorefining operations, where partial removal of hemicelluloses from wood or pulp would be implemented in an existing kraft pulp mill.

1.2 Aims and scope of the thesis

This dissertation work aims to investigate the effect of various hemicellulose extraction processes for partial removal of hemicelluloses from wood and pulp material on the properties of paper-grade kraft pulp fibers.

More precisely, three alternative methods for the partial removal of hemicelluloses from wood and pulp material were studied. The objective was to clarify the fiber characteristics and the properties of paper manufactured from hemicellulose-extracted fibers. The hemicellulose extraction concepts studied were (1) a softwood chip pretreatment process prior to kraft pulping, (2) alkaline extraction of bleached birch kraft pulp, and (3) enzymatic treatment, xylanase treatment in particular, of bleached birch kraft pulp. Together with the characterization of the properties of the hemicellulose-extracted fibers the two latter hemicellulose-extracted pulps were utilized in a pilot-scale papermaking environment in order to evaluate the upscalability of the concepts.

This research provides new insights on the opportunities to utilize hemicellulose-extracted fibers for modern papermaking purposes and sheds light on the possibilities to create more valuable and innovative end products from these specialty fibers. The work is limited mostly to the fiber and papermaking properties of hemicellulose-extracted pulps. Detailed analysis on the composition of co-product streams obtained by the studied methods for the partial removal of hemicelluloses from wood and pulp and evaluation of the techno-economical feasibility of the hemicellulose extraction concepts are outside the scope of this work.

1.3 Outline

The experimental part and Papers I-IV give the details of the work carried out. These papers discuss (1) the hemicellulose extraction processes and (2) characteristics of the hemicellulose-extracted paper-grade pulps. In addition to a summary of the work carried out in Papers I-IV, the experimental part of the thesis contains some earlier unpublished results.

2 HEMICELLULOSE EXTRACTION

2.1 Hemicelluloses

Hemicelluloses are, after cellulose, the second most abundant biomass polysaccharide in the world and they comprise about one third of wood material (see Table I). Other chemical components in the wood material are lignin, extractives, inorganics, and polysaccharides other than cellulose and hemicelluloses. (Sjöström 1993)

Table I General chemical composition of softwood and hardwood (Alén 2000) and more detailed chemical composition of pine (*Pinus sylvestris*) and birch (*Betula pendula*) as described in Sjöström (1993).

Wood species	Cellulose, %	Hemicelluloses, %		Other polysaccharides, %	Lignin, %	Extractives, %	Inorganics, %
		GGM	Xylan				
Soft-wood	40	25-30		0-5	25-30	4-6	<0.5
<i>Pinus sylvestris</i>	40	16.0	8.9	3.6	27.7	3.5	0.3
Hard-wood	40	30-35		0-4	20-25	2-4	<0.5
<i>Betula pendula</i>	41	2.3	27.5	3.4	22.0	3.2	1.4

The term *hemicellulose* was originally proposed by Schulze (1891) to designate the polysaccharides extractable from plants by aqueous alkali. Initially, these polysaccharides were mistakenly believed to represent an intermediate material of the biosynthesis of cellulose. However, it turned out that these polysaccharides represent a distinct and separate group of plant polysaccharides and later in the 20th century many other terms, such as *polyoses*, *cellulosans*, *polyuronides*, and *non-cellulosic carbohydrates* were proposed for hemicelluloses by several researchers (Wise 1949). However, the term *hemicellulose* is still valid today and several reviews on the chemistry and biochemistry of hemicelluloses are available (see e.g., Scheller and Ulvskov 2010; Pauly et al. 2013).

Hemicelluloses designate the cell-wall polysaccharides of land plants, excluding cellulose, other miscellaneous polysaccharides (starch, callose, l-arabinan, xyloglucan, fucoxylglucan, and rhamnoarabinogalactan), and pectin components (galactouronans, galactans, and arabinan). Hemicelluloses in their natural form are generally water-insoluble, alkali-soluble

substances that are more readily hydrolyzed by acid than cellulose. However, some hemicelluloses, such as fragments of hardwood xylan and the arabinogalactan found especially in larch species are partly or even totally water-soluble. Structurally, hemicelluloses differ from cellulose in that they are branched and have much lower molecular weights, i.e., degree of polymerization (DP). For hemicelluloses the DP is on average between 100 and 200, whereas for native cellulose it is around 10000. Unlike cellulose, hemicelluloses have a random and amorphous structure. Thus, the chemical and thermal stability of hemicelluloses is lower than that of cellulose. (Sjöström 1993; Alén 2000)

In general, the hemicellulose fraction of woods comprises a collection of polysaccharide polymers, polymers consisting of several different kinds of pentoses (D-xylose and L-arabinose), hexoses (D-mannose, D-glucose, and D-galactose), and deoxyhexoses (e.g., L-rhamnose). Small amounts of sugar acids (4-*O*-methyl-D-glucuronic acid, D-galacturonic acid, and D-glucuronic acid) can also be present. Hemicelluloses consist of more than one type of these sugar units and are sometimes referred to in terms of the sugars they contain, for example, galactoglucomannan (GGM), arabinoglucuronoxylan (AGX), arabinogalactan (AG), glucuronoxylan (GX), and glucomannan (GM). The proportion and chemical composition of hemicelluloses differ in softwoods and hardwoods, while cellulose is a relatively uniform component of all wood species. (Sjöström 1993; Alén 2000)

2.1.1 *Softwood hemicelluloses*

The major constituents of the hemicelluloses in softwoods are GGMs (15-20% odw), and AGX (5-10% odw). The former contain a backbone polymer of D-glucose and D-mannose. The backbone of GGM is a linear or slightly branched chain of β -(1 \rightarrow 4)-linked D-mannopyranose (β -D-Manp) and D-glucopyranose (β -D-Glcp) units. D-galactopyranose (α -D-Galp) residues are linked as single-unit side chains by α -(1 \rightarrow 6) bonds. GGM in softwood can be roughly divided into two types: one with low galactose content (10-15% odw), and the other with high galactose content (5-8% odw). The low-galactose fraction has a ratio of galactose:glucose:mannose of about 0.1:1:4 and the high-galactose fraction has a ratio of 1:1:3. In both cases, the acetyl content is about 6% of the total GGM, i.e., the C₂-OH and C₃-OH positions of the backbone polymer have acetyl groups substituted on them an average of every three to four hexose units. Often, the two forms of GGM are simply called glucomannan. (Sjöström 1993; Alén 2000)

2.1.3 Differences between hardwood and softwood hemicelluloses

Although the hemicelluloses in softwoods and hardwoods are fairly similar, there are distinct structural differences. Softwood hemicelluloses have a high proportion of mannose units and more galactose units than hardwood hemicelluloses, whilst hardwood hemicelluloses have a high proportion of xylose units and more acetyl groups than softwoods. Furthermore, softwood xylans differ from hardwood xylans by the lack of acetyl groups and, unlike hardwood xylans, softwood xylans contain α -L-Araf side units. In addition to the aforementioned, hemicelluloses from both softwoods and hardwoods also contain other polysaccharide groups, usually present in minor quantities. These might be important components for the living tree, but are of little interest when considering the technical applications. Table II summarizes the main structural features of hemicelluloses appearing in both softwoods and hardwoods. (Sjöström 1993; Alén 2000)

Table II The major hemicellulose components in softwood (SW) and hardwood (HW). Modified from Sjöström (1993).

Wood type	Hemicellulose type	Amount (% odw)	Composition			Solubility	DP ²
			Units	Molar ratios ¹	Linkage		
SW	Galacto-glucomannan	5-8	β -D-Manp β -D-Glcp α -D-Galp Acetyl	3 1 1 1	1 \rightarrow 4 1 \rightarrow 4 1 \rightarrow 6	Alkali, water ³	100
	(Galacto)-glucomannan	10-15	β -D-Manp β -D-Glcp α -D-Galp Acetyl	4 1 0.1 1	1 \rightarrow 4 1 \rightarrow 4 1 \rightarrow 6	Alkaline borate	100
	Arabino-glucuronoxylan	5-10	β -D-Xylp 4-O-Me- α -D-GlcpA α -L-Araf	8 2 1	1 \rightarrow 4 1 \rightarrow 2 1 \rightarrow 3	Alkali, DMSO ³ , water ³	100
HW	Glucuronoxylan	15-30	β -D-Xylp 4-O-Me- α -D-GlcpA Acetyl	10 1 7	1 \rightarrow 4 1 \rightarrow 2	Alkali, DMSO ³	200
	Glucomannan	2-5	β -D-Manp β -D-Glcp	1-2 1	1 \rightarrow 4 1 \rightarrow 4	Alkaline borate	200

¹Approximate values, ²On average, ³Partial solubility

SW=softwood, HW=hardwood, p=pyranose, f=furanose, Me=methyl, Man=mannose, Glc=glucose, Gal=galactose, Ara=arabinose, Xyl=xylose, and GlcpA=glucuronic acid.

2.2 Hemicellulose extraction alternatives

In the pulp and paper industry, the removal of hemicelluloses from wood is currently being carried out commercially in the production of dissolving-grade pulps, which can be further processed into regenerated fibers or cellulose derivatives. Because of the very low hemicellulose content (<10%), the intermediate fiber product is unsuitable for paper or paperboard manufacture (Sixta 2006). However, the partial hemicellulose extraction processes, such as the near-neutral green liquor process for hemicellulose extraction, have already been implemented on industrial scale also in paper-grade pulp manufacturing (Pendse 2009; van Heiningen et al. 2011). The motivation for such an approach is the co-production of hemicellulose-extracted pulp and hemicellulose-based chemicals or fuels.

In an IFBR approach with co-production of paper-grade pulp and hemicellulose-based chemicals, the hemicelluloses could be recovered from the side streams or process waters of the chemical pulping process. In such cases, the hemicellulose content of the produced pulp remains unchanged as the hemicellulose removal processes are separate from the main production line. Another way to recover hemicelluloses would be to tailor the hemicellulose content of the pulp and to produce a hemicellulose co-product stream for further processing by integrating a hemicellulose extraction process with an existing fiberline. This in effect would influence the existing pulping process and properties of the produced pulp, namely the hemicellulose content of the pulp. The hemicellulose content in paper-grade kraft pulp has traditionally been controlled by using yield-enhancing and carbohydrate-preserving pulping additives; anthraquinone (AQ), polysulfide (PS), and/or sodium borohydride (NaBH_4) (Kettunen et al. 1982; Li et al. 1998; Vaaler 2008). However, if the aim is to integrate the hemicellulose extraction process with an existing fiberline, the hemicellulose removal will have direct effects on the pulp yield, processability, selectivity of hemicellulose removal, and the properties of the produced fibers. Hence, clarifying the properties of the hemicellulose-extracted fibers is of great importance for the process economy in a sustainable IFBR.

Several studies on the effect of different hemicellulose extraction processes on various isolated aspects of the fiber line, and fiber and papermaking properties of the produced pulp have been published (discussed in Chapters from 2.2.1 to 2.2.3).

In addition, several possibilities for exploiting the extracted hemicelluloses fraction have been reported. Traditionally, industrial utilization of xylan for instance has mainly concentrated on its conversion into furfural and xylitol, yet much more versatile use of this biopolymer is possible (Deutschmann and Dekker 2012). Furthermore, apart from using hemicelluloses and their derivatives for papermaking purposes (Watson et al. 1956; Schmorak and Adams 1957; Hannuksela et al. 2004; Ren et al. 2009; Köhnke et al. 2010; Silva et al. 2011), application areas such as films and barrier coatings (Plackett and Hansen 2008; Mikkonen and Tenkanen 2012), hydrogels (Gabrielii and Gatenholm 1998; Willför et al. 2008; Meenaa et al. 2011), biopolymer derivatives (Kisonen et al. 2012; Petzold-Welcke et al. 2014), food additives and nutraceuticals (Moure et al. 2006; Sedlmeyer 2011; Aachary and Prapulla 2011), and even pharmaceuticals (Ebringerová et al. 2008; Daus and Heinze 2010) have recently been seen as potential end uses for hemicellulose-based products. In addition, the extracted hemicelluloses can serve as a platform chemical for various end uses (Saha 2003; Carvalheiro et al. 2008; Peng et al. 2011). The molecular composition and end-use possibilities for extracted hemicelluloses are greatly dependent on the hemicellulose removal concept applied.

2.2.1 Value prior to pulping (VPP) concept

The value prior to pulping (VPP) concept, i.e., the concept of hemicellulose extraction from pulpwood prior to pulping along with the conversion of the extracted carbohydrates to ethanol or other value-added chemicals, has been reviewed as an effective approach for integrating biorefining operations into an existing mechanical or chemical pulp mill. Various ways to extract wood hemicellulose from wood chips prior to kraft pulping has been extensively investigated by the pulp and paper industry (Richter 1956; Rydholm 1967a). Recently, hemicellulose extraction technology has attracted renewed interest as a means to separate hemicelluloses for biofuels or biochemicals production in combination with paper-grade pulp production by kraft pulping process. In such an approach, the residual wood material after hemicellulose extraction would be used in the conventional kraft pulping process. Therefore, the production of special-grade pulps, in which some of the hemicelluloses are not desired, would be possible.

To date, several methods for the extraction of hemicelluloses prior to the pulping process have been reported. Hemicelluloses can be extracted from wood chips prior to pulping by alkaline treatment (Al-Dajani et al. 2009; Helmerius et al. 2010; Júnior et al. 2013), near-neutral extraction (Mao et al. 2008; Marinova et al. 2009; van Heiningen et al. 2011; Lundberg et al.

2012), or by prehydrolysis. In a prehydrolysis process, the hemicelluloses are hydrolyzed to oligomeric and monomeric sugars with the aid of, for example, pressurized hot water (autohydrolysis) (e.g., Casebier et al. 1969; Carrasco and Roy 1992; Garrote and Parajo 2002; Yoon et al. 2008; Al-Dajani et al. 2009; Leschinsky et al. 2009; Testova et al. 2011), dilute acids (e.g., Parajó et al. 1994; Frederick et al. 2008; Al-Dajani et al. 2009), or steam (e.g., San Martín et al. 1995). While the main focus of the early studies on the prehydrolysis process was on producing high quality dissolving-grade pulp for viscose rayon, opportunities have been described for producing hemicellulose-extracted paper-grade kraft pulp with the pre-extracted hemicellulose stream as a co-product (Kenealy et al. 2007). Such wood chip pretreatment processes for the co-production of paper-grade pulp and a hemicellulose stream as a prehydrolysate for chemical upgrading have recently also been studied for chemi-mechanical pulp (Liu et al. 2012ab; Hamzeh et al. 2013), and mechanical pulp processes (Bilek et al. 2011; Houtman and Horn 2011; Jaaidi and Stuart 2011; dos Santos Muguet et al. 2013). Interestingly, the wood prehydrolysis process is reviewed not only as an opportunity for dissolving pulp and/or paper-grade pulp producing mills, but also as a pretreatment for improving biomass combustion quality (Pu et al. 2011, 2013; Treasure et al. 2012; Runge et al. 2013), wood fiber properties in wood plastic composites (Hosseinaei et al. 2012; Pelaez-Samaniego et al. 2013ab) and particleboard production in terms of dimensional stability of the product (Paredes et al. 2008).

The attraction of these kinds of approaches is the integrated production of wood fiber or pulp and renewable biofuels and/or chemicals from the extracted hemicelluloses, i.e., prehydrolysate. Hemicellulose recovery is the first step in producing value-added products from the prehydrolysate. Lignin, extractives, and other contaminants should be separated from the prehydrolysate, which makes its separation and purification of great importance. Several studies emphasize the significance of the purification and isolation of polysaccharides from the prehydrolysate. Processes such as adsorption (Gütsch and Sixta 2011), filtration (Koivula et al. 2011), ethanol precipitation (Liu et al. 2011), laccase-induced lignin polymerization (Wang et al. 2014), and flocculation (Shi et al. 2012) have been described for contaminant removal and isolation of polysaccharides prior to upgrading the product to biofuels and/or chemicals. In addition, the separated lignin itself can be a raw material for many value-added products (Schorr et al. 2014), e.g., phenols, biofuel, and biocomposites. Two potential pathways for hemicellulose recovery are presented in Figure 4. For the techno-economical

feasibility of producing prehydrolysis-kraft pulp targeted for high volume paper and paperboard production, the quality and yield of the produced pulp ought to be maintained.

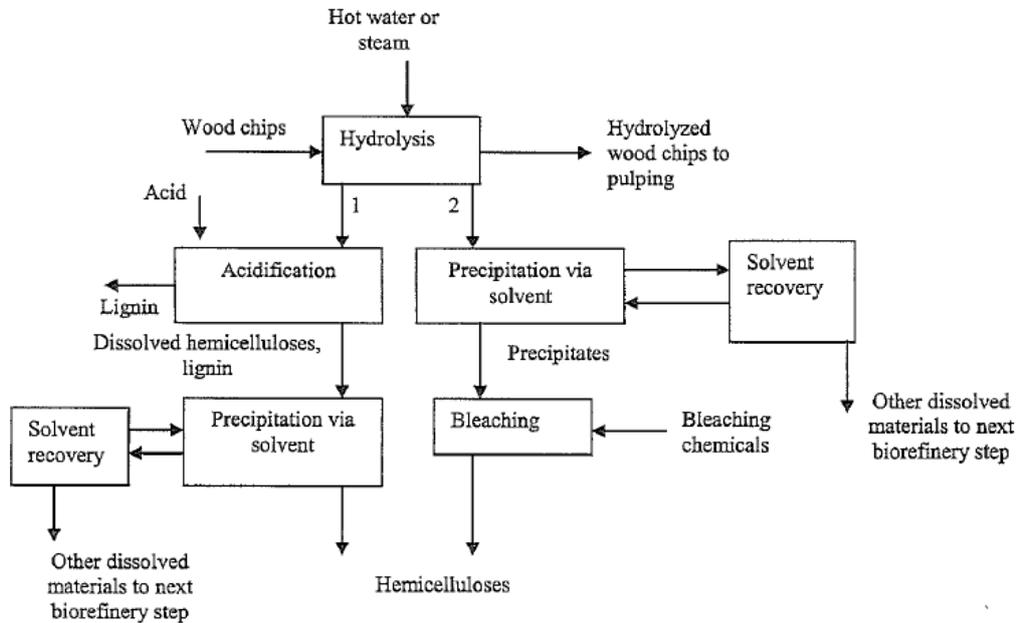


Figure 4 Proposed flow diagram of hemicellulose recovery from prehydrolysate (Fatehi and Ni 2011).

2.2.2 Treatments for bleached kraft pulp

As mentioned previously, the predominant type of hemicelluloses in hardwoods is GX. Thus, an existing fiber line producing bleached hardwood kraft pulp represents an attractive source for the production of polymeric xylan on industrial scale. Xylan, as polymeric or oligomeric sugars, could also be recovered from hardwood material by alkaline wood chip pretreatment prior to pulping (Al-Dajani et al. 2009; Helmerius et al. 2010; Júnior et al. 2013). However, when a xylan product of high purity is targeted, the extraction of xylan from bleached hardwood pulp seems to be the most reasonable option, as no expensive purification steps are needed to remove the lignin and other contaminants present in the extract.

2.2.2.1 Alkaline extraction of bleached birch kraft pulp

Hemicellulose removal by alkaline extraction using sodium hydroxide (NaOH) has been studied for agricultural residues, such as wheat bran and barley husks (Bataillon et al. 1998; Höjje et al. 2005). The dissolved hemicelluloses can then be concentrated and purified by ultrafiltration (Krawczyk et al. 2011, 2013), and used, e.g., for the production of thermoplastic

xylan derivatives (Jain et al. 2001) and oxygen barrier films for food packaging (Sternemalm 2008; Zhang et al. 2011b). A somewhat similar alkaline extraction and xylan recovery process with product upgrading is also applicable for bleached hardwood kraft pulp.

Bleached birch kraft pulp is a potential source of xylans, because it contains about 25% of hemicellulose (Talja et al. 2009). Consequently, an existing fiber line producing bleached hardwood, especially birch, kraft pulp represents an attractive source for the production of xylan on industrial scale. Alkaline extraction of xylan from bleached kraft pulp has been mainly studied for the upgrading of paper-grade hardwood kraft pulps into dissolving-grade pulps by combining alkaline extraction and enzymatic treatment steps for thorough hemicellulose removal (Ibarra et al. 2009, 2010; Köpcke et al. 2010; Gehmayr et al. 2011). However, the alkaline extraction of xylan from bleached birch kraft pulp for papermaking purposes might provide significantly improved industrial profitability by offering new sources of revenue from the new material stream: polymeric xylan.

It has been reported that the alkaline extraction of xylan from bleached birch kraft pulp yields a high molar weight xylan in a pure polymeric form (Pekkala 2008; Fuhrmann and Krogerus 2009), which might be advantageous in terms of the further processing of xylan. In addition to the utilization of the extracted xylan stream in-situ or for high-value chemicals production, this process allows simultaneous production of special-grade papermaking birch kraft pulp with low xylan content. However, the alkali concentration during extraction must be controlled well to avoid cellulose crystallinity conversion from native cellulose (cellulose I) into cellulose II. Thus, the obtained alkaline-extracted fiber product with decreased xylan content would still be suitable for paper or paperboard manufacturing. It has been reported (Wallis and Wearne 1990; Gomes et al. 2014) that by keeping the alkali (NaOH) concentrations under 6-7% (i.e., 1.5-1.75 M), no conversion from cellulose I to cellulose II occurs with chemical pulps. Alkaline-extracted bleached kraft pulp fibers could be a valuable raw material in some existing pulp and paper applications, such as fluff pulp (Lund et al. 2012) or tissue paper (Gomes et al. 2014), or in novel niche applications with high-value end use, such as raw material for the preparation of nanocellulose (Pönni et al. 2014). The process description for alkaline extraction of xylan from bleached birch kraft pulp with co-production of alkaline-extracted and a purified xylan product is depicted in Figure 5.

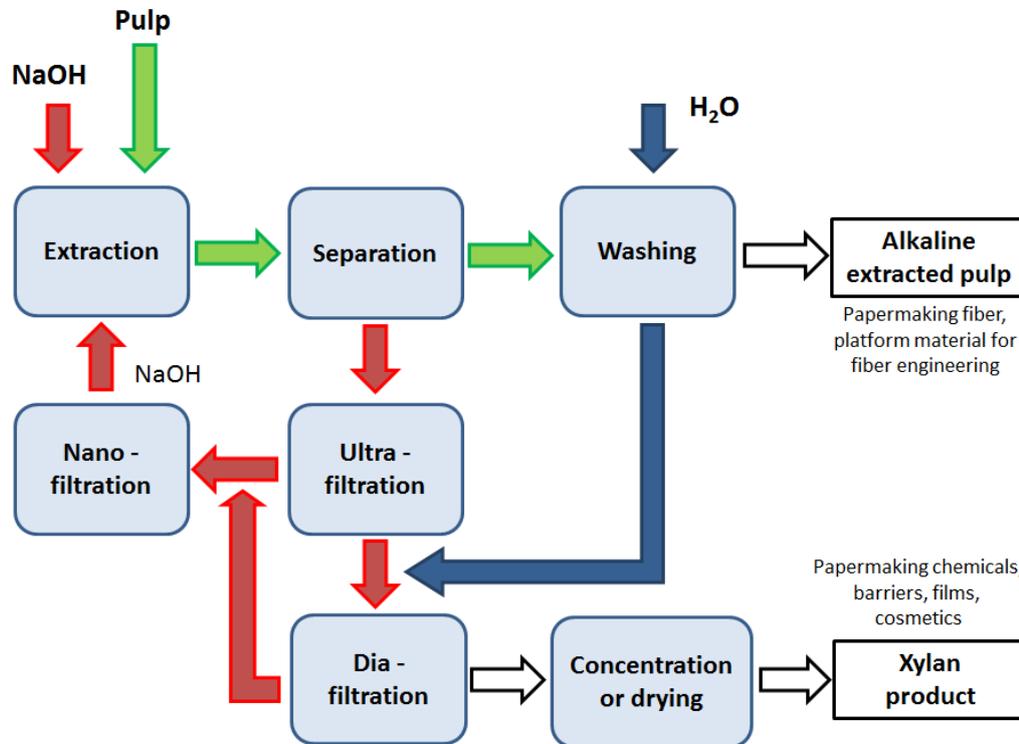


Figure 5 Process description of alkaline extraction of bleached birch kraft pulp, modified according to Fuhrmann and Krogerus (2009), Talja et al. (2009), and Varhimo et al. (2014).

2.2.2.2 Xylanase treatment of bleached birch kraft pulp

The number of studies on fiber modification with enzymes such as cellulases and hemicellulases/cellulases mixtures is vast (Bajpai 2012). Xylanases belong to the group of hemicellulases. The main focus of xylanase utilization in pulp and papermaking has been on bleach boosting (Viikari et al. 1994a; Bajpai 2004) and enhancing the refining efficiency of kraft pulp (Noe et al. 1986; Kibblewhite and Clark 1996; Oksanen et al. 1997a; Dickson et al. 2000; Mansfield et al. 2000) or chemi-mechanical pulp (Lei et al. 2008, 2012; Yang et al. 2011). Recently, Hakala et al. (2013) described thorough xylan removal from bleached hardwood kraft pulp by combining alkaline extraction and xylanase treatment steps to obtain polymeric xylan and xylooligosaccharides (XOs) as valuable side streams in dissolving-grade pulp production. XOs are currently produced mainly from agricultural feedstocks rich in xylan but wood-based raw materials have also been considered for XO production (Moure et al. 2006). Compared to xylan-derived biorefining co-products such as xylose for fermentation or polymeric xylan for films, barriers, and hydrogels, XOs could be attractive high-value

chemical compounds owing to their pharmaceutical and nutraceutical properties (Aachary and Prapulla 2011). Consequently, XOs could also provide an interesting high-value co-product in a biorefinery concept where selective modification of the carbohydrate composition of bleached hardwood paper-grade pulp rich in xylan is performed by means of hemicellulase enzymes. Partial or selective removal of hemicellulose from paper-grade hardwood kraft pulp by enzymatic treatment, xylanase treatment in particular, enables tailoring of the papermaking properties of the pulp (Blomstedt et al. 2010).

2.2.3 Other alternatives

In addition to VPP concepts and treatments for bleached kraft pulp for partial removal of wood hemicelluloses, several other possibilities for hemicellulose recovery from the side streams and process waters of chemical pulping processes have been described: from early cooking liquor (Axelsson et al. 1962; Axegard et al. 2009), weak black liquor (Axelsson et al. 1962; Danielsson 2014), black liquor hydrolysate (Mesfun et al. 2014), or from Lignoboost filtrates (Lundqvist et al. 2009; Wallmo et al. 2009). In these cases, the hemicellulose content of the produced pulp remains unchanged as the processes are separated from the main production line. However, the impurities, particularly lignin, present in these side streams of the pulping process can reduce the recovery efficiency and post-processability of the recovered hemicelluloses.

Furthermore, mechanical pulp process waters have been reviewed as an alternative to recover glucomannan for further modification (Willför et al. 2003ab; Persson et al. 2007; Xu et al. 2008). In addition to the use of glucomannan derivatives in papermaking (Lindqvist et al. 2013), end use in applications such as hydrocolloids (Willför et al. 2008), oil-in-water emulsion stabilizers (Mikkonen et al. 2009), bioactive polymers in food and pharmaceutical applications (Ebringerová et al. 2008), or starting material for the production of functional polymers (Mikkonen et al. 2010) have been investigated for the recovered glucomannan stream.

3 EFFECT OF HEMICELLULOSES ON FIBER AND PAPER PROPERTIES

Hemicelluloses contribute to the mechanical properties of kraft pulp fibers and to the paper properties, although quantitatively hemicelluloses are significantly less abundant in the paper-grade pulp fibers than cellulose. It has been known for a long time that the hemicellulose content of the fibers has some effect on kraft pulp quality (e.g., Young and Rowland 1933; Ratliff 1949; Cottrall 1950; Spiegelberg 1966; Rydholm 1967b). High concentrations of hemicellulose on the surface of paper-grade kraft pulp fibers have some well-established benefits regarding the papermaking properties of the fibers: improved beatability (Cottrall 1950; Centola and Borruso 1967; Bhaduri et al. 1995; Silva et al. 2011), improved bonding potential and strength properties (Rydholm 1967b; Schönberg et al. 2001; Hannuksela et al. 2004), and reduced drying-induced hornification (Oksanen et al. 1997b; Köhnke and Gatenholm 2007; Köhnke et al. 2010). Evidently, a lot of information can be found from the existing literature on the effect of hemicelluloses on fiber and paper properties, although the hemicellulose content in the pulp has been varied quite inconsistently between the different studies. However, some of the impacts relating to the hemicellulose content on fiber and paper properties could well be regarded as generalized effects, and these properties are discussed below for fiber (Chapter 3.1) and paper properties (Chapter 3.2).

3.1 Fiber characteristics

The importance of hemicelluloses on fiber properties has traditionally been interpreted as a contribution to the swelling tendency of the papermaking fiber. Young and Rowland (1933) found a relationship between the swelling behavior and the hemicellulose content of the chemical pulp. Since then, numerous studies on the swelling tendency and water absorption capacity of chemical pulp fiber have been conducted (Scallan 1983). Increased swelling and water absorption capacity of pulp fibers with high hemicellulose content is attributed to the strong water-binding tendency of hemicelluloses.

The hemicellulose content of pulp has been reported to have an influence on drying-induced hornification (Oksanen et al. 1997b; Cao et al. 1998; Rebuzzi and Evtuguin 2006; Moss and Pere 2006). Köhnke and Gatenholm (2007) and later Köhnke et al. (2010) suggested that hornification could also be reduced by adsorbing birch xylan on chemical pulp fibers. Adsorption of xylan increased the fiber swelling, specific fiber surface area, and wet fiber

flexibility of once-dried and rewetted fibers. It has been suggested that the mechanism of hornification depends on an increase in the degree of cross-linking between cellulose fibrils, or interfibril aggregation, caused by additional hydrogen bonds formed during drying, which are not broken in rewetting (Weise 1998). Hemicelluloses can prevent hornification and partially restore the swelling capacity of dried fibers by impeding the strong bonding of adjacent fibrils during water removal from the interfibrillar cavities of the cell wall. Furthermore, the cellulose fibril aggregate dimensions in never-dried and dried fibers increase as the hemicellulose content in the fibers decreases (Hult et al. 2001; Pönni et al. 2012).

As mentioned above, hemicelluloses contribute significantly to the fiber-water interactions of both never-dried and dried fibers. Consequently, hemicelluloses are responsible for the ease of pulp beating, since the swelling tendency of the fiber facilitates the beating action. The increased hydration of the fiber surface layer and the resultant effects on the fiber plasticity in water, fiber-to-fiber and fiber-to-metal friction increase the beating response of fibers with high hemicellulose content. Thus, shorter beating times and less energy absorption in beating is a feature of kraft pulps with high hemicellulose content (Cottrall 1950; Centola and Borruso 1967; Rydholm 1967b; Hunger 1983; Young 1994; Vaaler 2008; Yoon and van Heiningen 2008) and can also be achieved by the addition of hemicelluloses to the stock prior to beating (Centola and Borruso 1967; Bhaduri et al. 1995; Silva et al. 2011; Han et al. 2012).

As the chemical composition of kraft pulp and the specific role of hemicelluloses are important for the fibrillation process, hemicelluloses also play a role in achieving nanofibrillation by the mechanical treatment of pulp. Iwamoto et al. (2008) studied the effect of hemicelluloses on chemical pulp nanofibrillation and discovered that low hemicellulose content in once-dried pulp prevented fibrillation down to nanosized (10-20 nm wide) fibrils. These observations are related to the increased interfibril aggregation during the drying of pulp with low hemicellulose content. Strongly bound cellulose fibrils in dried pulp are difficult to separate from each other if some of the hemicelluloses are removed from pulp before drying. However, Iwamoto et al. (2008) showed that if a pulp with low hemicellulose content was microfibrillated in never-dried form, it fibrillated almost as well into nanosized fibrils as the never-dried reference pulp. It thus appears that a large amount of hemicelluloses facilitate nanofibrillation of pulp and improve efficiency in the production of cellulose nanomaterials, especially for once-dried pulps. Hemicelluloses can also stabilize fibers (Hannuksela et al. 2004; Rojas and Hubbe 2004; Huber et al. 2012) and nanofibrils (Arola et

al. 2013) against flocculation in suspension similarly to mucilage gums (Rojas and Hubbe 2004).

The hemicellulose content influences the deformation tendency of the fibers (Page et al. 1985a). According to Brännvall and Lindström (2007), softwood fibers with high xylan content are able to endure mechanical treatment better than fibers with lower xylan content as the latter have more local fiber wall defects. Rauvanto et al. (2006) reported similar findings for enzymatically treated softwood fibers: xylan acted as a protective component against fiber deformation during oxygen delignification. It appears that fibers with low hemicellulose content are more susceptible to mechanically induced damage and local fiber cell wall defects. Some aspects of the effects of the hemicellulose content of pulp on fiber properties are summarized in Table III.

Table III Some aspects of the effects of the hemicellulose content of pulp on fiber properties.

Property	Low hemicellulose content	High hemicellulose content	Explanation / Other
Beatability		Better	The presence of hemicelluloses facilitates the fiber fibrillation process during beating due to increased hydration of the fiber
WRV and FSP		Higher	Increased swelling and water retention can be attributed to the strong water-binding tendency of the hemicelluloses
Hornification	Intensified		Hemicelluloses prevent hornification and partially restore the swelling capacity of dried fibers by impeding the strong bonding of adjacent fibrils during water removal from interfibril cavities
Fiber damage and deformations	Higher		Fibers with low hemicellulose content are more susceptible to mechanically induced damage and local fiber wall defects
Nano-fibrillation		Improved	Pulp with high hemicellulose content fibrillates more easily into nanosized fibrils by mechanical treatment
Fiber flocculation		Lower	Hemicelluloses stabilize fibers and nanofibrils against flocculation

3.2 Paper characteristics

Firstly, the adverse effect of high hemicellulose content on the tear index of paper has been clearly established in several studies (Cottrall 1950; Richter 1956; Spiegelberg 1966; Rydholm 1967ab; Hunger 1983; Kettunen et al. 1982; Page et al. 1985b; Schönberg et al.

2001; Molin and Teder 2002; Bronkhorst and Bennett 2002a; Hannuksela et al. 2004). High hemicellulose content in pulp gives a low tear index for paper sheets. When paper is torn, the fibers are either fractured or peeled off from each other. In pulp with low hemicellulose content, the fiber-to-fiber bonding is decreased and fibers are peeled off from each other rather than fractured when a sheet is torn (Amidon 1981). Peeling off fibers from each other requires more energy than fracturing the fibers. Consequently, the energy needed for tearing a paper sheet made from high hemicellulose content pulp is lower than that made from low hemicellulose content pulp (Bronkhorst and Bennett 2002a). The observations made by Molin and Teder (2002) on more fractured and broken fibers in the fracture zones for pulps with higher hemicellulose content after tearing are in accordance with this theory.

Secondly, a decrease in the tensile index is also considered to be a major feature of low hemicellulose content pulps (Page et al. 1985b; Molin and Teder 2002). In addition, paper made from pulp with higher hemicellulose content shows a higher tensile stiffness index (TSI) compared to handsheets made from pulp with lower hemicellulose content. The TSI of paper, defined as the maximum angular coefficient in the stress-strain curve of the paper, is mainly affected by the amount of fiber-to-fiber bonds (Giertz and Rodland 1979), i.e., the stronger the fiber-to-fiber bonding, the higher the maximum angular coefficient. Furthermore, reduced fiber-to-fiber bonding has been reported to decrease tensile index values (Rydholm 1967b) and increase tear index values (Bronkhorst and Bennett 2002a). Therefore, it appears that many of the mechanical properties of paper made from pulp with low hemicellulose content are caused by the changes in fiber-to-fiber bonding. In addition to mechanical properties related to fiber-to-fiber bonding, the high hemicellulose content of kraft pulp has been reported to increase paper brittleness and decrease the folding number (Germgård et al. 1980; Molin and Teder 2002).

Thirdly, hemicelluloses also have an influence on other than mechanical characteristics of paper. High hemicellulose content of pulp may lead to more rapid aging and thus cause pronounced deterioration of properties during the artificial or natural aging of paper. Pulp or paper yellowing is often viewed as one of the early signs of the aging and deterioration of paper (Đurovič and Zelinger 1993; Carter 1996). Beelik (1967) reported that both cellulose and hemicellulose chains cleaved in the heat aging of pulp and hemicelluloses in particular contribute to the colors and acidity developed in heat-aged pulps. More recently, Zervos (2010) reported that hemicelluloses and their degradation products in paper aging actually

play a part in the oxidation of cellulose by initiating the production of reactive oxygen species. Theander and Nelson (1988) and Buchert et al. (1997) have shown that xylans contribute more to the formation of colored compounds than glucomannan in the heat-induced aging of chemical pulps. Furthermore, the formation of colored compounds and the yellowing effect of xylan have been demonstrated after the artificial aging of bleached kraft pulps (Buchert et al. 1997; Forsskahl et al. 1998). Thus, it seems likely that the aging and yellowing tendency of pulp is increased with higher content of hemicelluloses, xylan in particular. Optical properties (Hunger 1983) and the printability of paper with offset ink (Hu et al. 2013) have also been reported to be affected by the hemicellulose content of pulp. Some aspects of the effects of the hemicellulose content of pulp on paper properties are summarized in Table IV.

Table IV Some aspects of the effects of the hemicellulose content of pulp on paper properties.

Property	Low hemicellulose content	High hemicellulose content	Explanation / Other
Fiber-to-fiber bonding		Improved	Hemicelluloses work as an adhesive between the fibers
Tensile strength		Higher	A decrease in tensile index and an increase in tear index are considered to be the main features of low hemicellulose content pulps
Tear strength	Higher		
Paper brittleness		Higher	At low relative humidity levels high hemicelluloses content of pulp can cause low folding endurance due to the rigidity of the fiber-to-fiber bonding network
Optical properties	Higher opacity and LSC		Increased LSC and opacity also indicate decreased fiber-to-fiber bonding
Paper aging		Intensified	Hemicelluloses and their degradation products play a part in the oxidation of cellulose by initiating the production of reactive oxygen species
Brightness stability	Better*		Formation of colored compounds and pulp yellowing are decreased

*Glucomannan content might have a negligible effect on brightness stability according to Buchert et al. (1997).

4 EXPERIMENTAL WORK

4.1 Structure of the experimental work

Three hemicellulose extraction processes to partially remove hemicelluloses from wood and pulp material were studied: (1) a softwood chip pretreatment process prior to kraft pulping, (2) alkaline extraction of bleached birch kraft pulp, and (3) enzymatic treatment, xylanase treatment in particular, of bleached birch kraft pulp. Figure 6 depicts the potential location in the fiberline of the alternative hemicellulose extraction concepts.

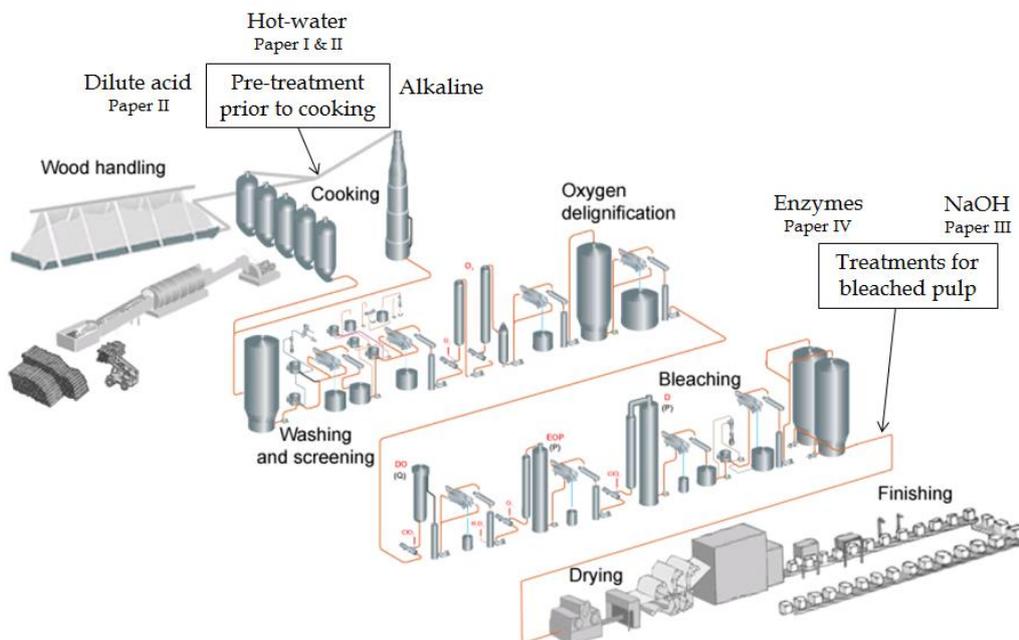


Figure 6 Hemicellulose extraction alternatives studied in the experimental part and their potential location in the fiberline: (1) pretreatments prior to cooking, and (2) treatments for bleached kraft pulp. Modified from Knowpulp (2014).

4.2 Materials and methods

The experimental methods applied in this work are summarized here. More detailed descriptions are given in Papers I-IV.

4.2.1 Pretreatments prior to kraft pulping (Paper I and II)

The objective of this sub-project was to treat pulpwood chips prior to pulping to remove the hemicellulosic carbohydrate material therein in an appropriate form to be utilized for the production of ethanol. At the same time, the bulk of the fiber material was subjected to alkaline cooking to produce prehydrolysis-kraft pulp. If the extracted hemicelluloses were hydrolyzed to monomeric sugars and fermented to ethanol, wood chip pretreatment prior to pulping would allow for the co-production of pulp and bioethanol. This in effect would transform a pulp mill into a pulp and biofuel-producing forest biorefinery.

The main results concerning bleachability and the papermaking properties of pretreated pine kraft pulps with some aspects of pulping will be presented within this work. The potential applications for the pretreatment extracts (prehydrolysates) and techno-economical evaluations of the studied wood chip pretreatment concepts are given elsewhere (e.g., Kautto et al. 2010; Sainio et al. 2013). Figure 7 presents a block diagram of the prehydrolysis concepts with red lines illustrating the process streams studied in this work.

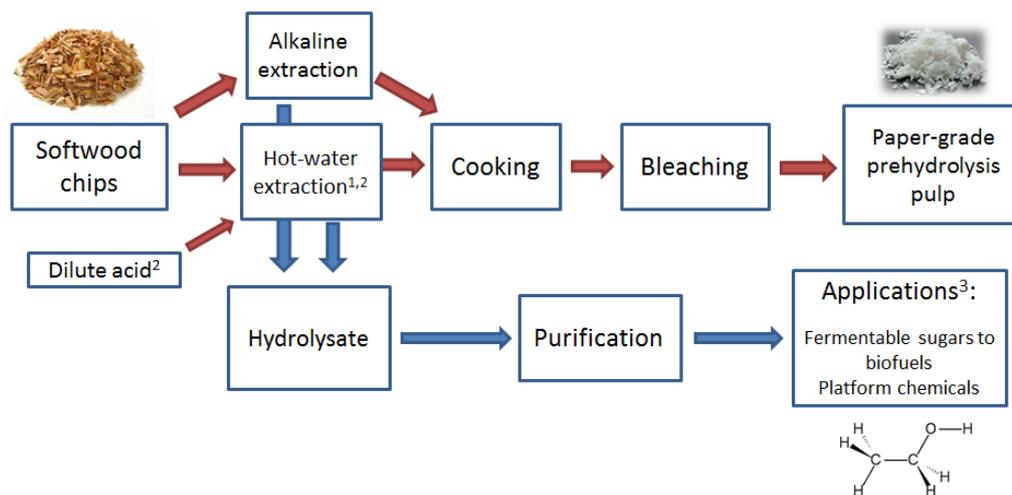


Figure 7 Wood chip pretreatment processes prior to kraft pulping. ¹=Paper I, ²=Paper II, ³=Viikari and Alén (2011).

4.2.1.1 Pretreatments and kraft pulping

In the pretreatment studies, pressurized hot-water (**PHW**), dilute-acid prehydrolysis (**AcidH**), and alkaline pre-extraction (**AlkE**) methods were compared for screened (Ø7mm+ Ø13mm) pine (*Pinus sylvestris* L.) wood chips. In addition, a PHW process (**Pulp 2** and **Pulp 3**) for

industrial screened ($\text{\O}7\text{mm} + \text{\O}13\text{mm}$) pine (*Pinus sylvestris* L.), possibly including some spruce (*Picea abies*), pulpwood chips was studied. After draining the hydrolysis liquor (undiluted prehydrolysate) from the digester, the pretreated wood chips were subsequently cooked and bleached. There was no intermediate chip washing between pretreatments and cooking. Based on earlier studies for softwood (Chirat et al. 2009; Kautto et al. 2010), hardwood (Chirat et al. 2012), eucalyptus (Sixta 1996), and sugar maple pulp (Amidon et al. 2006), the pretreated wood chips were cooked with a reduced cooking time (H-factor) to achieve the target kappa number. The wood chip pretreatment and cooking conditions for the reference (**Ref** and **Pulp 1**) and pretreated pulps are shown in Table V.

Table V Process conditions in the hemicellulose extractions.

Wood chip pretreatments						
Test Point		P-factor ¹	Time, min	Temperature, °C	Liquid-to-wood ratio, L/kg	Chemical charge
Group 1	Pulp 1 ²	-	-	-	-	-
	Pulp 2 ²	200	128	150	4.6	-
	Pulp 3 ²	200	128	150	4.6	-
Group 2	Ref ³	-	-	-	-	-
	PHW ³	200	128	150	4.6	-
	AcidH ³	80	67	150	4.6	0.5% H ₂ SO ₄ (odw)
	AlkE	-	240	80	4.6	25% alkali (odw)
Cooking						
Test Point		Temperature, °C	Liquid-to-wood ratio, L/kg	Effective alkali, % (odw)	Sulfidity, %	H-factor
Group 1	Pulp 1 ²	150	4.6	20.0	40	1600
	Pulp 2 ²	150	4.6	20.0	40	1000
	Pulp 3 ²	150	4.6	20.0	20	1300
Group 2	Ref ³	160	4.6	20.0	35	1600
	PHW ³	160	4.6	20.8	35	1250
	AcidH ³	160	4.6	20.8	35	1250
	AlkE	160	4.6	22.0	35	1200

¹determined according to Sixta (2006), ²Paper I, ³Paper II.

4.2.1.2 Bleaching and pulp testing

After cooking, test points Pulp 1, 2, and 3 (**Group 1**) and test points Ref, PHW, AcidH, and AlkE (**Group 2**) were oxygen delignified (O₂) to a target kappa of 16±1 and 15±1, respectively. Group 1 pulps were bleached (DED) to a target ISO brightness of 74% and beaten in a PFI mill (ISO 5264-2:2002), whereas Group 2 pulps were bleached (DED) to a target ISO brightness of 88% and beaten in a Voith Sulzer laboratory refiner with a specific

edge load (SEL) of 2.5 J/m (filling 3-1.0-60C). Handsheets were prepared (ISO 5269-1:1998) with different degrees of beating and the CSF values of the stocks were measured (ISO 5267-2:2001). The fiber morphology of Group 2 pulps was evaluated with an automated optical fiber analyzer (Kajaani FS-300, Metso Automation) and water retention values (WRV) were determined according to SCAN-C 62. Pulp bleaching conditions are shown in Table VI.

Table VI Bleaching conditions with chemical charge amounts.

Process variable	Test point	O ₂ ¹	D ₀	E	D ₁
Temperature, °C	Group 1	90	60	60	70
	Group 2	90	60	70	70
Time, min	Group 1	30	45	75	180
	Group 2	60	60	60	180
Pulp consistency, %	Group 1	10	10	10	10
	Group 2	12	9	10	9
Pressure, bar	Group 1	5	-	-	-
	Group 2	8	-	-	-
Act. Cl charge, %	Group 1	-	0.20 × incoming kappa	-	1
	Group 2	-	0.24 × incoming kappa	-	*
NaOH charge, %	Group 1	2	-	0.6 × D ₀ charge	-
	Group 2	Ref 1.45	-	0.35 × D ₀₋ charge	0.12 × D ₁₋ charge (for pH adjustment)
		PHW 1.35			
		AcidH 1.21			
AlkE 1.70					

*determined so that target brightness was attained, ¹0.5% of Epsom salt was added in the O₂ stage.

4.2.2 Alkaline extraction of bleached kraft pulp (Paper III)

The objective of this sub-project was to investigate the effects of alkaline extraction of bleached birch kraft pulp on the papermaking properties of the pulp. Alkaline extraction with a mild aqueous sodium hydroxide (NaOH) solution was used to partially liberate xylan from the fibers. The effects of alkaline extraction time on the xylan dissolution rate and quantity and the papermaking properties of the extracted pulp were investigated. Furthermore, both the non-extracted and alkaline-extracted bleached birch kraft pulp fiber material was applied in traditional papermaking as a part of the fiber furnish in order to evaluate the possibilities of mixing alkaline-extracted and non-extracted fibers for paper manufacture. Figure 8 presents a block diagram of the alkaline extraction concept with red lines illustrating the process streams that were studied within this work. Potential applications for the alkaline-extracted xylan

product from bleached birch kraft pulp have been investigated elsewhere (e.g., Pohjanlehto et al. 2011; Kataja-aho et al. 2012; Laine et al. 2013; Alekhina et al. 2014).

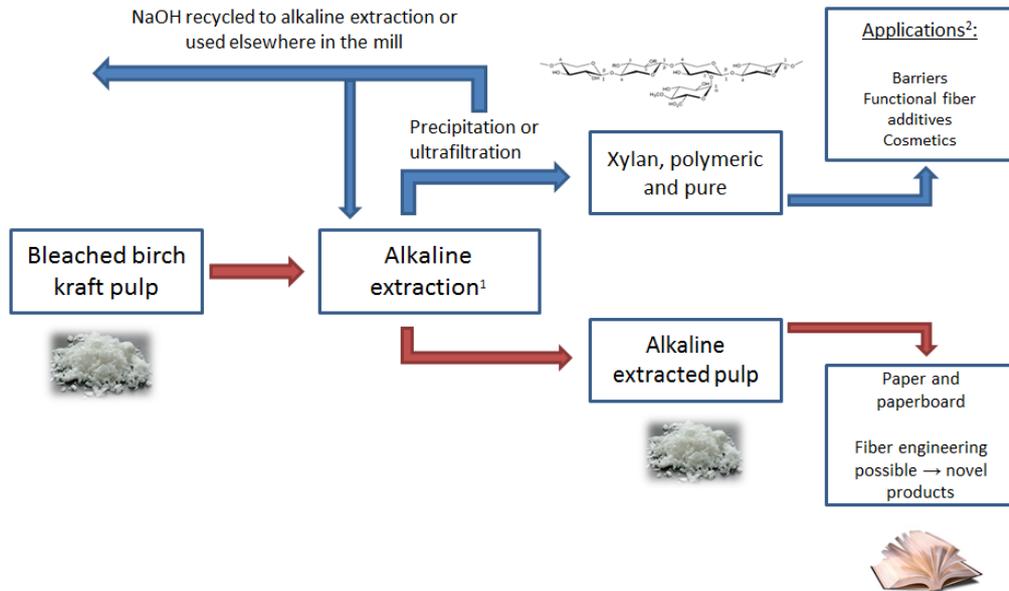


Figure 8 Alkaline extraction of xylan from bleached birch kraft pulp. ¹=Paper III, ²=Deutschmann and Dekker (2012).

4.2.2.1 Raw material preparation and testing

Industrial dried elementary chlorine free (ECF) bleached birch kraft pulp containing 74.6% cellulose, 24.9% xylan, and 0.5% glucomannan, determined according to SCAN-CM 71:09, was obtained from a Finnish pulp mill. The alkaline extraction was done in a 30 m³ extraction vessel for 665 kg of odw pulp with a NaOH concentration of 0.56 M, temperature 24.1°C, pulp consistency 2.6%, and extraction time of 60 minutes. After the extraction time, the pulp was immediately washed using a MicraScreen equipped with a screen plate having 100 micron openings. The pulp washing was continued until the pH of the pulp suspension was below 10. The details of the alkaline extraction procedure can be found in Paper III.

The effects of the alkaline extraction time on xylan dissolution and the fiber and papermaking properties of the extracted pulp were studied by pulp sampling after 5, 10, 20, 30, 45, and 60 minutes of extraction. The pulp samples were washed in a Büchner funnel with tap water until the pH of the filtrate was below 8. This was done in order to remove the NaOH residues and dissolved carbohydrates from the fiber suspension.

The total organic carbon (TOC) content in the first filtrates from the Büchner filtrations was determined using a Shimadzu TOC-5050A analyzer. The washed pulp cakes were subsequently tested for their xylose-to-glucose ratio (XGR), water retention value (WRV), and Schopper-Riegler number ($^{\circ}$ SR), determined according to standard methods SCAN 71:09, ISO 5351:1, SCAN-C 62, and SCAN-C 19:65, respectively. The fiber properties were determined using an optical fiber analyzer (Kajaani FS-300, Metso Automation) and the preparation of handsheets and testing of paper properties was performed according to ISO 5269-1:1998 from pure pulp samples without any addition of chemicals.

4.2.2.2 *Use of alkaline-extracted fibers in pilot-scale papermaking*

The papermaking and paper properties of alkaline-extracted and non-extracted birch kraft pulp were expected to be markedly different, based on the literature regarding the effects of hemicellulose content in kraft pulp fibers on their physico-chemical properties (see Chapters 3.1 and 3.2). Therefore, mixtures of alkaline-extracted and non-extracted bleached birch kraft pulp were tested in a pilot-scale papermaking environment, to ascertain whether they possess interesting properties compared to those that the pulps have alone.

The non-extracted and alkaline-extracted pulps were refined to $^{\circ}$ SR 22 using a pilot-scale disc refiner. The specific energy consumption (SEC) required to reach this $^{\circ}$ SR level was 26 and 59 kWh/tn for non-extracted and alkaline-extracted pulp, respectively. Paper with grammage of 75 g/m² was made on a pilot paper machine under controlled process conditions. The refined pulps were used as such or as mixtures to prepare stocks for a pilot paper machine. The mixing ratios of the pulps used in the pilot paper machine are given in Table VII. The pilot paper machine was running at a speed of 60 m/min and in addition to non-extracted and alkaline-extracted pulp, precipitated calcium carbonate (24%), cationic starch (5.5 kg/tn), alkyl ketene dimer (1.5 kg/tn), and two component retention systems (150 g/tn cationic polyacryl amide and 1.5 kg/tn bentonite) were used in the furnish. The precise process conditions of the pilot-scale papermaking process are described in Lyttikäinen et al. (2014).

Table VII The mixing ratios of non-extracted and alkaline-extracted pulp in pilot trial.

Alkaline-extracted : non-extracted pulp ratio	0:100	25:75	50:50	75:25	100:0
Alkaline-extracted pulp, %	0	25	50	75	100
Non-extracted pulp, %	100	75	50	25	0

The paper web was also online surface-sized with starch (Raisamyl 21221) on a size press unit and the dried paper was machine-calendered by applying different levels of nip pressure (0, 15, and 30 kN/m). Finally, the non-calendered and calendered paper was reeled and cut into sheets to determine the paper properties according to SCAN and ISO standards.

4.2.3 Xylanase treatment of bleached kraft pulp (Paper IV)

The objective of this sub-project was to selectively remove the surface xylan and simultaneously modify the carbohydrate composition of refined never-dried birch kraft pulp by xylanase treatment and to utilize the xylanase-treated pulp in papermaking. Xylanase treatment of the bleached birch kraft pulp fibers was done in order to obtain a papermaking fiber having a high cellulose concentration on the surface of the fiber and xylanase hydrolysis products, XO's in particular, as a valuable co-product stream. Figure 9 presents a block diagram of the enzymatic treatment concept with red lines illustrating the process streams that were studied within this work. The potential applications for the XO's derived from hardwood such as birch have been described elsewhere (e.g., Falck et al. 2013)

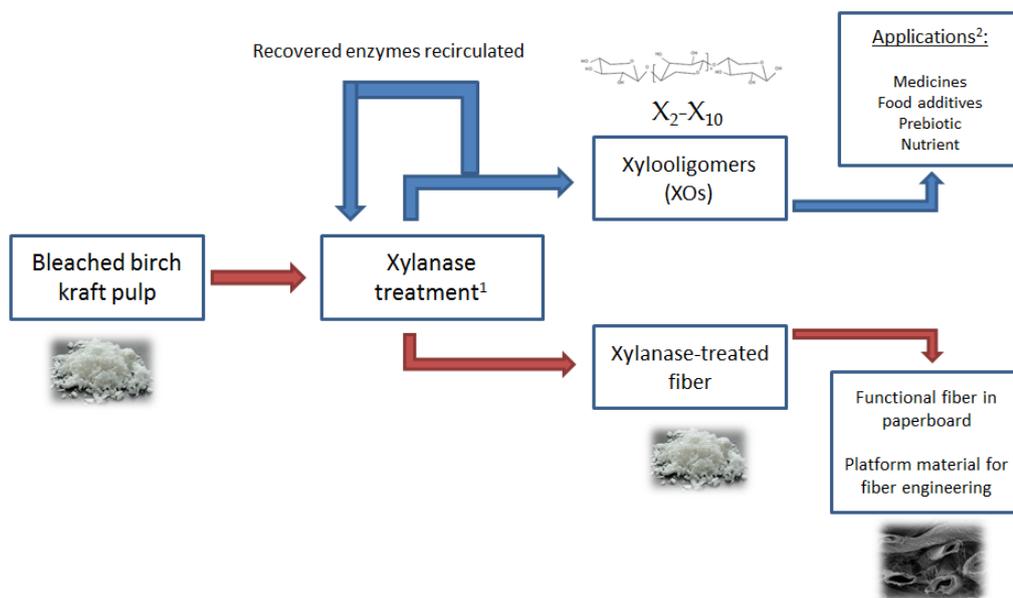


Figure 9 Enzymatic (xylanase) treatment of bleached birch kraft pulp. ¹=Paper IV, ²=Aachary and Prapulla (2011).

4.2.3.1 *Raw material preparation and testing*

An industrial never-dried ECF-bleached birch kraft pulp containing 74.6% cellulose, 24.9% xylan, and 0.5% glucomannan, determined according to SCAN-CM 71:09, was obtained from a Finnish pulp mill and used as a raw material for the xylanase treatments (an endo-1,4- β -xylanase Shearzyme 500 L, Novozymes A/S, Denmark) in order to selectively remove xylan from the outermost fiber layers. In order to activate the fiber surface for better accessibility of xylanase, the pulp was refined to $^{\circ}$ 24 prior to xylanase treatment, using a pilot-scale disc refiner with a SEC of 32 kWh/tn. Xylanase treatment was done in a 5 m³ extraction vessel for 165 kg of odw pulp at 50°C for 90 minutes with an enzyme dose of 15 kg/tn of odw pulp, corresponding to 890 nkat xylanase/g of dry pulp. Prior to xylanase treatment, the pH of the pulp suspension (3.3% consistency) was adjusted to 5 with a dilute solution of sulfuric acid (H₂SO₄). The xylanase treatment conditions used in this study were selected based on a previous study by Metsämuuronen et al. (2013), in order to achieve a high XO yield in the dissolved carbohydrates. After 90 minutes of xylanase treatment, the enzymes were deactivated by heating the pulp suspension from 50°C to 90°C at a rate of 1.0° C/min and keeping it at that temperature for over 30 minutes. The details of the xylanase treatment procedure can be found in Paper IV.

The effects of xylanase treatment time on xylan dissolution and the fiber and papermaking properties of the xylanase-treated pulp were studied by pulp sampling after 10, 20, 30, 60, and 90 minutes of treatment time. In order to remove the denaturated enzyme residues and the dissolved carbohydrates from the stock, the xylanase-treated pulp was dewatered on a pilot paper machine without any chemical dosing. The paper web was dried with air and recovered as a wet lap pulp at a dry matter content of approximately 35%. As the $^{\circ}$ SR decreased from 24 to 17 due to the xylanase treatment, a similar dewatering procedure on a pilot paper machine was followed for the untreated reference pulp, which was refined to $^{\circ}$ SR 17 using a pilot-scale disc refiner with a SEC of 9 kWh/tn. The xylanase-treated (**XT pulp**) and reference (**R pulp**) wet lap pulps were reslushed with a wet disintegrator according to standard ISO 5263-1. The pulp preparation and sample labeling procedure is depicted in Figure 10.

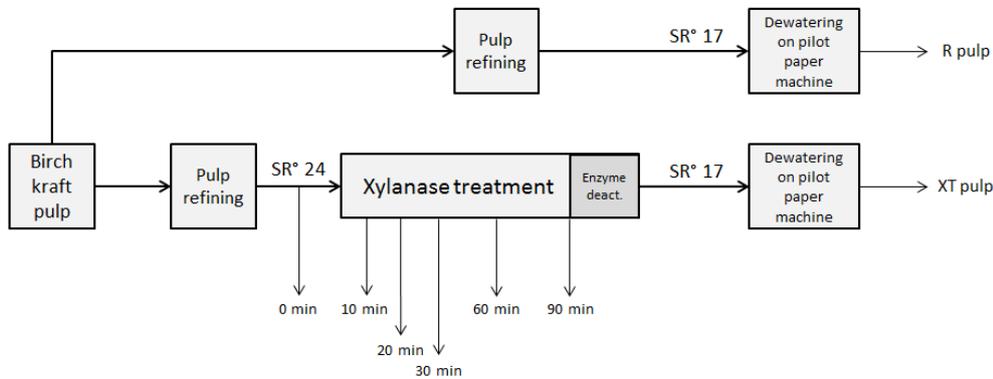


Figure 10 The xylanase-treated pulp preparation procedure.

The pulp samples were washed in a Büchner funnel with hot tap water in order to remove the enzyme residues and dissolved carbohydrates. The carbohydrates dissolved in the pulp filtrates were determined from the first filtrates from the Büchner filtrations according to Sundberg et al. (1996). The ratio of mono- and oligosaccharides was not studied in detail in this study. However, according to Metsämuuronen et al. (2013), bleached birch kraft pulp treated with endo- β -1,4-xylanase (Shearzyme 500 L) in similar conditions releases XOs, particularly xylobiose and xylotriose, at moderately high concentrations, whereas the proportion of xylose in the dissolved carbohydrates is small.

The condition of the ultrastructure of the fibers was determined using both scanning electron microscopy (SEM) and atomic force microscopy (AFM). The sample preparation technique adopted prior to both SEM and AFM characterization was rapid freezing (cryofixation) of the semi-wet handsheets in liquid nitrogen (N_2), followed by overnight freeze-drying in order to prevent drying-induced hornification (Weise 1998). This procedure was inspired by earlier work that studied the ultrastructure of kraft pulp fibers in the never-dried state by SEM (Daniel and Duchesne 1998; Duchesne et al. 2001) and interfacial properties by AFM measurements (Fahlén 2005). The pulp WRV, wet zero-span tensile strength (WZST), and $^{\circ}$ SR were determined according to standard methods: SCAN-C 102 XE, ISO 15361, and SCAN-C 19:65, respectively. Fiber morphology was evaluated with an automated optical fiber analyzer (Lorentzen & Wettre, Sweden). The preparation of handsheets and testing of paper properties were performed according to ISO 5269-1:1998 from pure pulp samples without any addition of chemicals.

4.2.3.2 *Use of xylanase-treated fibers in pilot-scale papermaking*

The **R** and **XT** wet lap pulps were re-slushed with a vertical pulper and used as a raw material for papermaking. Paper with a grammage of 180 g/m² and end moisture content of 8% was made on a pilot paper machine under controlled process conditions from R and XT pulps. The pilot paper machine was running at 30 m/min and the paper web was machine-calendered with a nip pressure of 15 kN/m prior to reeling. In addition to R or XT pulp, cationic starch (5.5 kg/tn), alkyl ketene dimer (1.5 kg/tn), and two component retention systems (150 g/tn cationic polyacryl amide and 1.5 kg/tn bentonite) were used in the furnish. Finally, the non-calendered and calendered paper was reeled and cut into sheets to determine the paper properties according to SCAN and ISO standards.

5 RESULTS AND DISCUSSION

5.1 Pretreatments prior to kraft pulping (Papers I and II)

5.1.1 *Pulping and bleachability*

The acidic prehydrolysis processes (Pulp 2 and Pulp 3 for Group 1, and PHW and AcidH for Group 2 pulps) decreased the overall brownstock pulp yield on wood. It appeared that acidic pre-extraction of hemicelluloses prior to pulping led to rendering the remaining hemicelluloses in the wood more easily dissolvable in the subsequent alkaline cook, thus lowering the cooking yield. Adding a catalyst (H_2SO_4) increased the rate of dissolution of material from 11.5% to 14.2% during prehydrolysis. However, the more severe conditions in prehydrolysis caused by the addition of a catalyst can cause some cellulose degradation and even more pronounced alkaline degradation of the remaining carbohydrates in the subsequent cook, which was observed as further decreased yield on wood after cooking (Table VIII). An increase in wood consumption would have to be realized in order to obtain similar brownstock pulp production with a prehydrolysis process compared to the reference cook. Thus, from a techno-economical perspective, this would imply that potentially products much more valuable than biofuels would need to be produced from the prehydrolysate to compensate the rather significant increases in wood consumption.

In the cooking of Group 2 pulps, the pulp yield on wood of the reference cook (without wood chip pretreatment) was 46.9%. The pulp yields on wood after cooking of PHW and AcidH chips dropped by 4.8% and 7.4% from the value of the reference cook, respectively. However, the yield on wood after the cooking of AlkE chips was similar to that of the reference chips and caused only a minor reduction in hemicellulose content of the pulp compared to the reference (Table VIII). In this light, alkaline wood chip pretreatment could be an interesting option for the extraction of hemicelluloses prior to pulping since only those hemicelluloses are solubilized that would be dissolved during the initial phase of alkaline cooking. However, with the AlkE conditions presented in this study, the extracted carbohydrates can degrade to hydroxy acids. Hence, milder extraction conditions or other wood species (e.g., aspen, *Populus tremula*) could be more suitable if the aim is to recover the hemicelluloses as polymeric sugars by alkaline pretreatment (Al-Dajani and Tschirner 2008; Jun et al. 2012).

All the Group 2 pulps that were pretreated prior to kraft pulping were bleached to full brightness (ISO ~88%) in an (O)DED bleaching sequence with lower ClO₂ charges (calculated as total active chlorine, kg Cl/tn of pulp) than the unhydrolyzed reference pulp. In addition, prehydrolysis and cooking at a sulfidity level of 40% (Pulp 2) resulted in lower ClO₂ charges compared to the unhydrolyzed reference (Pulp 1) when bleaching pulp to a target ISO brightness of 74%. Similar reductions in the bleaching chemical consumption have been observed when comparing prehydrolyzed eucalyptus pulp to control kraft pulps (Colodette et al. 2011; Andrew et al. 2014). Lower chemical doses in bleaching would allow the possibility to improve the quality of bleaching effluents, when evaluated for their organic load (chemical oxygen demand, COD) and chlorinated organic values (adsorbable organic halogens, AOX). For Group 2 pulps, the contributing factors to the better bleachability of the prehydrolyzed pulps were a lower transition metal (Cu, Fe, and Mn) and hexenuronic acid content compared to the reference, see Appendix I. Chirat et al. (2013) have postulated that the structure of the remaining lignin could also contribute to the slightly better bleachability of prehydrolyzed softwood kraft pulp. Results concerning the bleachability of Group 1 and 2 pulps are presented in detail in Appendix I.

Table VIII Pulping and (O)DED bleaching characteristics of unhydrolyzed and prehydrolyzed pulps.

Property	Group 1			Group 2			
	Pulp 1	Pulp 2	Pulp 3	Ref	PHW	AcidH	AlkE
Yield of wood residue, %	100	Not determined		100	88.5	83.8	86.4
Hydrolysate pH, -	-	3.6	3.6	-	3.7	2.4	n.d.
Pulp after digester							
Kappa number	25.4	24.4	33.1	25.4	27.7	27.2	27.3
Residual alkali, g/L	7.9	9.8	10.5	8.0	9.1	8.1	11.0
Viscosity, mL/g	1280	1320	1280	1230	1330	1140	1260
Yield on wood, %	49.5	42.3	42.8	46.9	42.1	39.5	46.9
Pulp after O₂ stage							
Kappa number, -	16.1	13.6	16.4	15.3	15.1	13.4	15.6
Viscosity, mL/g	1060	1070	1010	1080	1100	1010	1060
ISO brightness, %	37.7	42.5	39.4	33.9	34.1	36.2	33.6
Yield on wood, %	48.5	41.5	41.6	46.3	41.2	38.6	46.0
Pulp after DED bleaching							
Viscosity, mL/g	1000	990	940	970	960	900	990
ISO brightness, %	74.1	73.7	71.9	87.6	87.1	87.8	87.6
Consumption of ClO ₂ , calculated as total act. chlorine (kg Cl per tonne of pulp)	42.2	37.2	42.8	60.2	59.0	49.3	59.0
Cellulose/hemicellulose ratio*	4.9	10.6	10.1	4.7	9.8	15.1	4.9

*Calculated according to Janson (1974).

5.1.2 Pulp and paper properties

5.1.2.1 Non-refined pulp

All of the non-refined pulp strength properties of the pretreated pulps were lower than those of the reference pulps. The TSI and Z-directional strength (Scott-Bond) values measured for Group 2 pulps indicated that the fiber-to-fiber bonding in the fiber network is reduced. In addition, the non-refined prehydrolysis-kraft pulp (PHW and AcidH) fibers were more curled and much more kinked than fibers in the reference pulp (Ref). It appears that, alkaline cooking preceded by prehydrolysis causes more clearly measurable angles (kinks) in the 3-dimensional fiber shape rather than just gently curling the fibers. Similar behavior was not observed with the alkaline pre-extracted pulp. The increased LSC and opacity also indicated decreased interfiber bonding in sheets made from the prehydrolyzed pulps, since increasing the interfiber bonding with fibrillar fines is known to have a decreasing effect on LSC (Luukko and Paulapuro 1999), and opacity is increased by decreasing interfiber bonding with debonding agents (Talaiepoor and Imani 2008). Consequently, the greater number of fiber deformations (Group 2 pulps) and the lower interfiber bonding due to the lower hemicellulose content in both Group 1 and 2 prehydrolysis-kraft pulps contributed to the loss in strength properties shown in Table IX.

Alkaline extraction of carbohydrates prior to pulping caused only a minor increase in the cellulose/hemicellulose ratio (increase from 4.7 to 4.9) of the pulp compared to the reference. Interestingly, the AlkE process caused changes in the fiber and paper properties of the non-refined pulp compared to the Ref, although the cellulose/hemicellulose ratio of these pulps was on quite a similar level. Thus, a wood chip pretreatment for hemicellulose removal, whether acidic or alkaline, has an impact on the physical properties of the non-refined pulp, yet the hemicellulose content of the bleached pulp would remain unchanged.

Table IX Fiber and paper characteristics of reference and pretreated non-refined pulps.

Property	Group 1			Group 2			
	Pulp 1	Pulp 2	Pulp 3	Ref	PHW	AcidH	AlkE
Cellulose/hemicellulose ratio*	4.9	10.6	10.1	4.7	9.8	15.1	4.9
Fiber length, mm	Fiber morphology and fiber-water interaction not determined			2.03	1.93	1.88	2.05
Fiber width, μm				25.6	25.0	24.6	25.5
Kink index, 1/m				820	1440	1660	770
Fiber curl, %				17.9	23.6	24.6	17.5
Fines content, %				2.7	2.5	2.2	2.5
Coarseness, mg/m				0.190	0.192	0.188	0.193
WRV, g/g				1.67	1.56	1.55	1.68
Apparent bulk density, kg/m^3	645	565	595	620	570	560	590
CSF, mL	710	705	710	710	720	715	710
Tensile index, Nm/g	45.8	23.5	26.5	34.2	19.0	19.2	28.9
Tear index, Nm^2/kg	21.7	15.0	16.5	21.3	14.8	13.3	18.2
Tensile stiffness index, kNm/g	5.6	3.3	4.0	4.7	3.0	3.0	4.0
Stretch, %	3.1	2.6	2.3	3.3	2.3	2.2	3.1
TEA index, J/g	1.06	0.47	0.47	0.87	0.34	0.33	0.70
Internal bonding strength, Scott-Bond, J/m^2	Not determined			168	127	112	142
Light-scattering coefficient, m^2/kg	26.9	33.1	31.9	31.3	34.8	38.1	31.0
Opacity, %	72.7	79.3	80.1	76.9	79.5	81.1	77.6

*Calculated according to Janson (1974).

5.1.2.2 Refined pulp

Table X shows that when the hemicellulose content in the bleached pulp was approximately halved by a prehydrolysis process prior to pulping (Pulp 2, Pulp 3, PHW), the required number of revolutions in a PFI mill (Group 1) and SEC in laboratory-scale low consistency refining (Group 2) to achieve a tensile index value of 70 Nm/g increased significantly. This could be attributed to the contribution of the hemicelluloses to the swelling tendency and increased hydration of the surface layer of fibers. With increased swelling, interfiber contact during beating increases the promotion of faster external fibrillation and hence a better beating response. When the hemicellulose content of the pulp was decreased to one third (AcidH) compared to the reference pulp (Ref), there was a 310% increase in SEC to reach a tensile index value of 70 Nm/g. It appeared that the slightly different beating action between the PFI mill and laboratory-scale low consistency refiner had a minor effect on the development of the prehydrolyzed pulp properties during pulp beating. The SEC in AlkE pulp beating was also increased to achieve comparable paper properties, e.g., a 33% increase to reach a tensile index level of 70 Nm/g compared to the reference pulp (Ref). The slightly

different hemicellulose content of the AlkE and Ref pulps was not likely to account for the entire change in the beating response. It is postulated that the physico-chemical changes of the fibers taking place during the wood chip pretreatment and subsequent alkaline pulping processes contribute to the experienced loss in beating response.

Table X Fiber and paper characteristics of refined reference and pretreated pulps. Values are interpolated to the given tensile index level of 70 Nm/g.

Property	Group 1			Group 2			
	Pulp 1	Pulp 2	Pulp 3	Ref	PHW	AcidH	AlkE
Cellulose/hemicellulose ratio*	4.9	10.6	10.1	4.7	9.8	15.1	4.9
Beating revs, - / SEC in beating, kWh/t	632	4780	3708	89	251	344	118
Fiber length, mm	Fiber morphology and fiber-water interaction not determined			2.07	1.92	1.57	2.09
Fiber width, μm				27.1	26.4	26.1	27.0
Kink index, 1/m				650	720	710	600
Fiber curl, %				17.1	18.5	16.8	16.9
Fines content, %				3.2	4.2	6.6	3.2
WRV, g/g				1.97	2.11	2.05	2.03
Apparent bulk density, kg/m^3	705	720	720	710	740	775	700
CSF, mL	680	620	635	575	370	285	525
Tensile index, Nm/g	70	70	70	70	70	70	70
Tear index, Nm^2/kg	15.6	19.8	20.5	14.9	15.9	13.0	15.1
Tensile stiffness index, kNm/g	7.1	6.7	7.2	6.9	7.0	7.1	6.5
Stretch, %	3.2	3.5	3.2	4.0	3.9	3.9	3.9
TEA index, J/g	1.60	1.70	1.60	1.95	1.94	1.98	1.89
Internal bonding strength, Scott-Bond, J/m^2	Not determined			386	533	344	365
Light-scattering coefficient, m^2/kg	22.3	21.7	22.0	23.6	23.2	25.2	22.1
Opacity, %	68.4	70.0	72.7	71.5	71.8	73.7	71.9

*Calculated according to Janson (1974).

Compared to the reference cooks, the papermaking properties of prehydrolyzed pulp (Pulp 2, Pulp 3, PHW), dilute-acid prehydrolyzed pulp (AcidH), and alkaline pretreated pulp (AlkE) as a function of sheet density were slightly reduced, severely reduced, and preserved, respectively. Alkaline pre-extraction of hemicelluloses from birch wood prior to pulping has also been shown to preserve the papermaking properties of kraft pulp (Testova et al. 2014). Evidently, the refining of Group 2 prehydrolysis-kraft pulps (PHW and AcidH) had straightened the fibers, since the difference in the amount of fiber deformations (kinks) was minor at a tensile index level of 70 Nm/g compared to the reference pulp (Ref). With the

exception of AcidH pulp, the tear index values at the corresponding tensile index for the pretreated pulps was higher than the reference. Consequently, these pretreated pulps had better strength potential (tensile index x tear index) than the unhydrolyzed reference pulp. The reinforcement index (RI) further indicates the reinforcing ability of chemical pulp and RI characterized by $T^*(l/w)$, where the ratio (l/w) of fiber length (l) and coarseness (w) is multiplied by the tear index of the pulp (T) at a given tensile index, normally 70 Nm/g or on a level used in a certain paper grade (Levlin 1991). PHW pulp had a slightly higher RI than the control pulp as a function of sheet density. This implied that with optimized process hot-water prehydrolyzed pulps could have potential as reinforcement pulp. However, the rather significant reduction in the beating response and strength development might present severe problems in the utilization of prehydrolyzed and alkaline pretreated pulps for papermaking purposes.

5.2 Alkaline-extracted birch kraft pulp (Paper III)

5.2.1 Xylan removal

Carbohydrate analysis revealed that the alkaline extraction of bleached birch kraft pulp was very selective towards xylan and, with a 60-minute extraction process carried out at ambient temperature, the NaOH concentration had an obvious increasing effect on the quantity of xylan removal (Table XI).

Table XI The relative carbohydrate composition of non-beaten fully bleached pulps determined according to SCAN-CM 71:09.

Chemical component	Non-extracted Pilot-scale 0.56 M NaOH	Alkaline-extracted Pilot-scale 0.56 M NaOH	Non-extracted Laboratory-scale 1.0 M NaOH	Alkaline-extracted Laboratory-scale 1.0 M NaOH
Cellulose	74.6	80.7	74.8	85.8
Xylan	24.9	18.7	23.6	13.0
Glucomannan	0.6	0.6	1.1	1.1
Total hemicelluloses	25.5	19.6	24.7	14.1
Cellulose/hemicellulose ratio*	2.9	4.1	3.0	6.1

*Calculated according to Janson (1974).

The duration of alkaline extraction of xylan from bleached birch kraft pulp with 0.56 M NaOH seemed to have a negligible effect on the amount of xylan extracted. In fact, the alkali

concentration was the only critical parameter in this type of hemicellulose extraction process. During the first 5 minutes of extraction, the XGR decreased by 37.5%, from 0.32 to 0.20, with a simultaneous pulp yield loss of 9.7% (odw). In the filtrate sample taken after 60 minutes of extraction time, the TOC content was 1.06 g/L. Presumably, over 99% of this TOC originated from the extracted xylan, and would therefore correspond to 63.1 kg of xylan in the filtrates, accounting for 9.5% of the studied birch kraft pulp and 38.1% of the xylan in this pulp. Both of these values were in agreement with the results from the determination of pulp XGR and yield loss after 60 minutes of extraction time. Thus, practically the same amount of xylan was extracted in 5 minutes as in 60 minutes, determined as pulp yield loss, XGR of the pulp, and TOC of the pulp filtrates (Table XII). These findings are in agreement with previous studies which have shown that the greatest decrease in xylan content due to alkaline extraction with 1.5-1.75 M NaOH occurs within the first minutes of the treatment (Scott 1984; Köpcke et al. 2010).

Table XII The effect of alkaline extraction time (5-60 min) on the xylose-to-glucose (XGR) ratio, total organic carbon (TOC) in the pulp filtrate, and the total yield loss with a basis of odw pulp. The yield loss of xylan is calculated based on the XGR.

Extraction time, min	0	5	10	20	30	45	60
XGR, -	0.32	0.20	0.21	0.21	0.21	0.21	0.20
TOC, g/L	n.d.	1.01	1.02	1.03	1.03	1.05	1.06
Pulp yield loss odw, %	-	9.7	7.3	7.0	7.4	7.8	8.1
Yield loss xylan, %	-	36.3	36.7	37.0	37.0	37.7	38.1

5.2.2 Pulp and paper properties

The WRV was affected by alkaline extraction. Hemicelluloses are the primary source of ionic groups in chemical pulp, and are also more hygroscopic and amorphous than cellulose. Thus, the WRV would be expected to decrease when the hemicelluloses are partially removed, as mentioned in Chapter 3.1. However, a 20.5% increase in pulp WRV was observed during the first 5 minutes of alkaline extraction, after which the WRV remained quite stable. For this reason, the results indicated that the penetration of alkali into the fiber cell wall takes place instantaneously during alkaline extraction. Furthermore, the more porous structure of the fiber wall caused by the NaOH and xylan leaching out from the fiber cell wall could lead to increased accessibility of the remaining charged ionic groups in the fiber wall to water. It is known that water is much harder to remove from intra- than inter-wall locations (Lai and

Scallan 1994). While the presence of the charged ionic groups in the fiber is a basic requirement for the pulp swelling, the nature of the counter ions of the ionic groups is also of great importance (Lindström and Carlsson 1982; Scallan 1983). Alkaline treatment increases the swelling of pulp fibers, and others have also found that extraction of hemicellulose from kraft pulp fibers with alkaline solutions increases the water absorptivity of the fibers (Fuhrmann and Krogerus 2009; Lund et al. 2012). Therefore, it is postulated that the location of the hemicelluloses remaining within the porous fiber wall after alkaline extraction together with possible ion exchange of the pulp to sodium (Na^+) form play an important role in determining the water binding capacity of alkaline-extracted kraft pulp fibers.

The alkaline extraction had slight time-dependent effects on the morphological character of the fibers (Table XIII). Firstly, the average length-weighted fiber length decreased from 0.985 mm to 0.970 mm during alkaline extraction. Secondly, the fiber width increased during alkaline extraction, which was likely due to the opening of the porous structure of the fiber wall caused by the NaOH and xylan leaching out from the fiber cell wall, rendering the fibers into a more swollen form. Thirdly, the alkaline extraction caused slight fiber deformations, which could be seen as an increase in the fiber form alternations in the transverse and longitudinal direction, i.e., curl and kink indices.

As shown in Table XIII, paper properties such as tear and tensile stiffness indices increased slightly at the beginning of extraction, and then decreased towards the end of extraction. The results indicated that a shorter extraction time could be slightly more favorable in terms of the paper properties of non-refined pulp. Detailed results on the fiber and paper properties as a function of alkaline extraction time are given in Paper III.

Table XIII The effect of alkaline extraction time (5-60 min) on selected fiber and paper properties. Standard deviations given in brackets.

Extraction time, min	0	5	10	20	30	45	60
WRV, g/g	1.17 (0.01)	1.41 (0.01)	1.38 (0.01)	1.40 (0.01)	1.41 (0.01)	1.42 (0.01)	1.41 (0.01)
Fiber length, mm	0.985	0.980	0.970	0.975	0.970	0.970	0.970
Fiber width, μm	16.0	16.0	16.1	16.1	16.1	16.2	16.1
Curl, %	11.2	11.3	11.3	11.5	11.8	11.8	11.9
Kink index, 1/m	730	730	780	800	780	810	820
Apparent bulk density, kg/m^3	680	690	695	695	690	690	685
Drainability, $^{\circ}\text{SR}$	21	20	20	20	20	20	20
Tensile index, Nm/g	42.5 (3.0)	42.0 (1.3)	43.1 (2.5)	41.6 (1.1)	42.1 (1.1)	39.7 (1.7)	41.2 (1.9)
Tear index, Nm^2/kg	7.4 (0.5)	8.0 (0.4)	8.2 (0.2)	7.4 (0.4)	7.9 (0.3)	7.0 (0.6)	6.9 (0.5)
Tensile stiffness index, kNm/g	6.3 (0.2)	6.5 (0.2)	6.6 (0.3)	6.2 (0.2)	6.5 (0.2)	6.3 (0.2)	6.4 (0.3)
Stretch, %	2.5 (0.3)	2.3 (0.1)	2.4 (0.2)	2.6 (0.2)	2.5 (0.2)	2.3 (0.2)	2.6 (0.2)
TEA index, mJ/g	766 (137)	720 (44)	778 (112)	800 (52)	778 (66)	679 (76)	787 (87)
Light-scattering coefficient, m^2/kg	32.4	33.2	32.2	33.1	32.7	32.8	32.9
Opacity, %	75.4	76.2	75.4	75.9	75.6	75.7	75.7

5.2.3 Papermaking in a pilot-scale environment

The pulp obtained after 60 minutes of alkaline extraction (0.56 M NaOH) and pulp washing was used as a raw material for papermaking. The contribution of the carbohydrate composition of bleached birch kraft pulp on wet-end chemistry and paper chemical retention has been discussed by Lyytikäinen et al. (2014).

5.2.3.1 Properties of non-surface-sized base paper

The incorporation of alkaline-extracted birch kraft pulp in the papermaking stock had some effects on the strength and structural/topographical properties on the 75 g/m^2 base paper produced. However, the results indicated that the addition of alkaline-extracted pulp in papermaking stock as a mixture with non-extracted pulp has a minor effect on the general properties of pulps with low hemicellulose content reported in the literature. A decreased tensile and tensile stiffness index together with an increased tear index have been reported to be the main features of low hemicellulose content pulps (see Chapter 3.2). Changes in these properties were clearly notable only when 75% or 100% of alkaline-extracted pulp was used

in the preparation of the papermaking stock. In particular, with a ratio of 25:75 of alkaline-extracted to non-extracted pulp, the change in the mechanical properties of paper was modest (Table XIV).

The interesting results obtained with the pulp mixtures could be due to the reinforcing effect of the non-extracted pulp in alkaline-extracted and non-extracted pulp mixture furnish, a phenomenon that is known from mixtures of mechanical and chemical pulps (Ritala 1987; Ritala and Huiku 1989). It seemed that when a pulp mixture contains non-extracted pulp, the non-extracted fibers are able to form a continuous load-carrying network and therefore no decrease is seen in tensile properties. However, if the portion of alkaline-extracted pulp was increased further to close to 100%, the load-carrying network of non-extracted fibers was lost. In addition, the different swelling properties of the two fiber types will have an effect on the activation of fibers during paper drying/consolidation, entailing additional effects on sheet bonding and strength properties with mixtures of alkaline-extracted and non-extracted pulps (Retulainen 1997). Lyytikäinen et al. (2014) demonstrated that reducing the xylan content in birch kraft pulp by alkaline extraction has a positive effect on the retention of papermaking chemicals. Thus, it must be noted that the process chemical doses were not changed during the trial and that the electrostatic charge of the fibers and the cationic demand of process waters differed between the studied pulps. Differing wet-end chemistry and chemical retention between the different pulp mixtures might have an effect on the determined paper properties. However, the properties of paper are a joint effect of the properties of the fiber raw material and their interactions with various papermaking chemicals. Thus, the results obtained for non-surface-sized base paper demonstrated that some amount of alkaline-extracted birch kraft pulp could be used in the papermaking stock without significantly losing physical or mechanical properties of the paper. Furthermore, the test points, i.e., various mixtures of alkaline-extracted and non-extracted pulps, showed no differences in pilot paper machine runnability and no web breaks were encountered during the trials.

Table XIV Non-surface-sized base paper properties of non-extracted and alkaline-extracted pulp mixtures. Values are geometric MD/CD means for strength properties and top/bottom side mean values for other tabulated properties. Standard deviations given in brackets.

Alkaline-extracted : non-extracted pulp ratio	0:100	25:75	50:50	75:25	100:0
Grammage, g/m ²	77.8	76.5	75.5	77.6	76.1
Bulk, cm ³ /g	1.58	1.59	1.68	1.61	1.56
Ash content, %	19.7	20.7	21.1	21.0	21.6
Bendtsen air permeance, $\mu\text{m}/\text{Pa s}$	32.3 (2.4)	36.5 (2.7)	34.8 (1.6)	32.2 (2.50)	38.8 (3.0)
Bendtsen roughness, mL/min	778 (71.1)	692 (72.7)	896 (75.9)	952 (69.7)	675 (45.9)
Stretch, %	1.79 (0.24)	1.92 (0.19)	1.89 (0.18)	2.38 (0.19)	1.99 (0.15)
Tensile index, Nm/g	28.0 (1.7)	27.4 (1.2)	28.0 (1.1)	26.4 (1.1)	24.8 (0.8)
Tensile stiffness index, kNm/g	4.35 (0.15)	4.14 (0.12)	4.18 (0.14)	3.77 (0.13)	3.80 (0.10)
TEA index, mJ/g	354 (66)	373 (57)	376 (50)	459 (57)	353 (40)
Tear index, mNm ² /g	4.9 (0.2)	4.7 (0.2)	5.3 (0.2)	5.2 (0.3)	5.0 (0.6)
Opacity, %	86.3	85.7	85.8	86.0	86.7
Light scattering co-efficient, m ² /kg	54.0	54.3	57.0	56.8	58.9
Cobb ₆₀ , g/m ²	68.5	37.4	35.3	36.4	43.1

5.2.3.2 Properties of surface-sized paper

Online surface sizing with a size press was difficult to run for some mixing ratios of non-extracted and alkaline-extracted pulp. No breaks were experienced with alkaline-extracted to non-extracted pulp mixing ratios of 0:100 and 100:0, and only a few web breaks were encountered with a ratio of 25:75. However, severe runnability problems in the form of web breaks were frequently experienced in the size press unit or in the drying section after surface sizing of paper with alkaline-extracted to non-extracted pulp mixing ratios of 50:50 and 75:25. This indicated changed physico-chemical properties of the wet and semi-dry web when the two raw material types, non-extracted and alkaline-extracted, were mixed.

The results presented in Figure 11 showed that no differences in the starch penetration or starch distribution in the paper of the surface-sized and calendered (15 kN/m) sheets were found between alkaline-extracted to non-extracted pulp mixing ratios of 0:100, 25:75, and 100:0. The dry strength enhancing effect of surface sizing decreased slightly when alkaline-

extracted fibers were included in the papermaking furnish. The results of all measured properties for the non-surface-sized base paper and surface-sized papers are reported in detail in Appendix II.

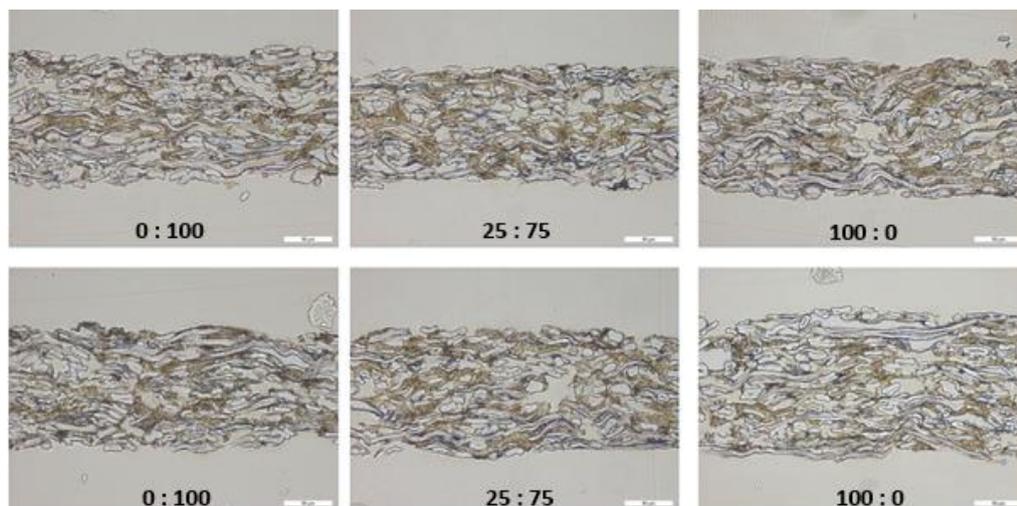


Figure 11 Images from surface-sized and calendered (15 kN/m) paper cross-sections after staining with iodine. Mixing ratios of alkaline-extracted to non-extracted birch kraft pulp 0:100, 25:75, and 100:0. Scale bar corresponds to 50 μm .

5.3 Xylanase-treated birch kraft pulp (Paper IV)

5.3.1 Xylan removal

The xylanase treatment of bleached birch kraft pulp dissolved carbohydrates from the fiber material (Table XV). The reference sample (0 minutes) contained small amounts (160 mg/L, corresponding to 0.47% of odw pulp) of dissolved carbohydrates. This was in accordance with values reported in the literature concerning carbohydrates dissolved during birch kraft pulp refining (Lindström et al. 1978). Table XV shows that almost a similar amount of xylan could be dissolved in 10 minutes compared to the amount obtained after 90 minutes of xylanase treatment, i.e., 2.8% (10 min) and 3.6% (90 min) of the original pulp dry weight was hydrolyzed. In addition, the amount of rhamnose and glucuronic acid released was 6.6 and 21.6 mg/L, respectively, after 10 minutes of xylanase treatment, after which their content in the pulp filtrate did not increase. Thus, it appeared that these side group residues bound to the birch xylan backbone were subjected to a rapid initial hydrolytic attack by the xylanase enzyme. Furthermore, the amount of carbohydrate components, apart from xylose, in the pulp filtrates decreased from 49.3 mg/L to 40.9 mg/L between 60 and 90 minutes of xylanase

treatment. This suggests that reprecipitation of the released hydrolysis products might occur after 60 minutes of xylanase treatment.

Table XV Dissolved carbohydrate components (mg/L) during xylanase treatment, analyzed as described in Sundberg et al. (1996).

Xylanase treatment time, min	0	10	20	30	60	90
Arabinose, mg/L	9.9	9	9.8	9.6	9.7	5.2
Rhamnose, mg/L	0.8	6.6	6.5	7.9	7.8	5.6
Xylose, mg/L	141.0	903.1	1035.9	1101.1	1173.3	1178
Glucuronic acid, mg/L	0	21.6	21.9	21	21.6	20.7
Galacturonic acid, mg/L	1.1	0	0.5	1.2	1.3	0
Mannose, mg/L	2.7	2.1	2.7	2.7	2.3	2.8
Galactose, mg/L	2.3	1.6	2.3	2.4	2.9	1.6
Glucose, mg/L	2	4.7	5.9	3.2	3.7	5
Released sugars, mg/L	-	788.8	925.7	989.3	1062.7	1059
Total dissolved carbohydrates, mg/L	159.8	948.5	1085.5	1149.1	1222.5	1218.7
Yield loss odw, %	0.47	2.78	3.18	3.37	3.58	3.57
Xylose content, %	88.2	95.2	95.4	95.8	96.0	96.7
Rhamnose content, %	0.5	0.7	0.6	0.7	0.6	0.5
Glucuronic acid content, %	0.0	2.3	2.0	1.8	1.8	1.7
Xylan-derived carbohydrates content, %	88.7	98.2	98.0	98.3	98.4	98.8

The vast majority (96.7%) of the total amount of dissolved carbohydrates after the 90-minute xylanase treatment of bleached birch kraft pulp was xylose, derived from the β -(1 \rightarrow 4)-linked xylopyranose (β -D-Xylp) backbone of xylan. Together with the 0.5% rhamnose and 1.7% glucuronic acid in the pulp filtrates based on the total dissolved carbohydrates, the amount of xylan-derived compounds could be estimated to be over 98.5% after 90 minutes of xylanase treatment. Therefore, the 3.6% of the original pulp dry weight dissolved after 90 minutes of xylanase treatment corresponded to 14.2% of the total amount of xylan, calculated from the 24.9% xylan content in bleached birch kraft pulp used as the raw material in this work. Based on a theoretical evaluation (Appendix III), the xylan content that is located in the outermost fiber layers, i.e., the primary cell wall (P) and outer secondary cell wall layer (S₁), of the bleached birch kraft pulp fibers used in this study, was approximately 15%. Hence, these results demonstrate that the commercial xylanase solution substantially free from cellulase activity was very surface-specific and could be used in the selective removal of surface xylan from the outermost fiber layers of refined never-dried bleached birch kraft pulp.

The interfacial properties of the fibers analysed with SEM and AFM further confirmed the surface- selective action of xylanase. The nano-scale fiber surface structures determined by AFM presented in Figure 12 showed the changes taking place in the never-dried fiber surface layer. The relatively smooth surface appearance present in the untreated reference samples (0 min) gradually disappeared during xylanase treatment. Such a change in the topography of the fiber can be attributed to the peeling process of the outermost fiber surface layer. Salmén and Burgert (2009) state that the secondary cell wall layers (S_1 , S_2 , and S_3) can be distinguished from the inclinations of the parallel-oriented cellulose fibrils with respect to the cell axis (cellulose microfibril angle, MFA); an outer S_1 having transversely oriented fibrils, S_2 with axially oriented fibrils, and an inner S_3 also with transversely oriented fibrils. Especially after 60- and 90-minute xylanase treatment times, the aligned surface microfibrils were clearly distinguishable from the 3-dimensional topography images. Thus, the AFM images presented in Figure 12 further implied that xylanase treatment is very surface-specific and that the xylose-based residues in the pulp filtrates have been released mainly from the fiber surfaces. This could be ascribed to the fact that the cellulose microfibrils aligned parallel to the fiber axis on the never-dried fiber surfaces become more visible in AFM images during xylanase treatment.

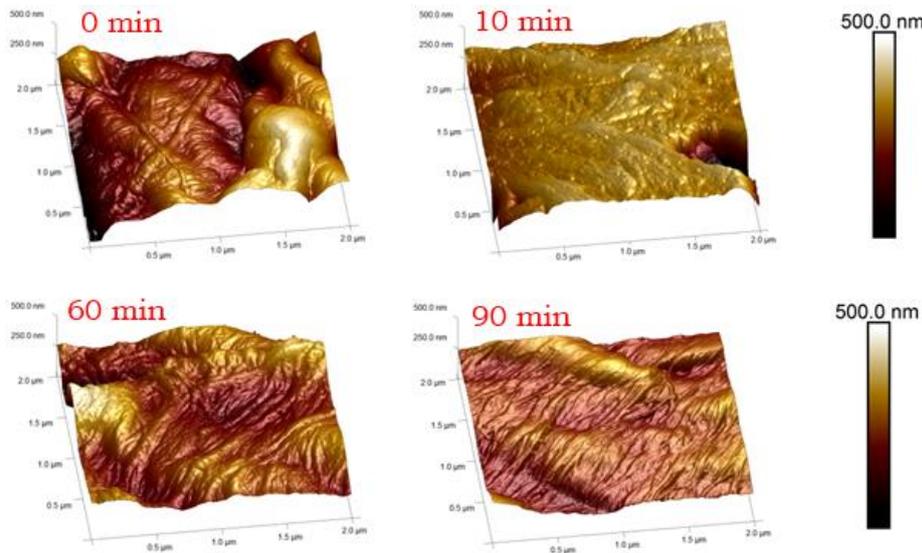


Figure 12 AFM images of 3-dimensional fiber topography (scan size $2\ \mu\text{m} \times 2\ \mu\text{m}$) of birch kraft handsheets after different xylanase treatment times.

5.3.2 *Pulp and paper properties*

Xylanase treatment increased the dewatering rate of the pulp and caused changes in the fiber morphology, with a slight decrease in fiber length and increase in clearly measurable angles (kinks) in the 3-dimensional fiber shape (Table XVI). The °SR decreased from 24 to 17 as xylanase acted on the fiber surface, removing the water-binding xylan. In addition, the xylanase might have acted preferentially on the high surface area fines fraction, which has a propensity to hinder dewatering by blocking interstices in the fiber network. Blomstedt et al. (2010) and Oksanen et al. (2009) also reported improved dewatering properties of xylanase-treated bleached hardwood kraft pulp. The WRV decreased from 212% to 195% during 90-minute xylanase treatment, which is in accordance with the studies reported by Oksanen et al. (1997b) and Moss and Pere (2006) on the xylanase treatment of non-refined never-dried bleached kraft pulp.

Du et al. (2012) have shown that the negative electrical charge of the fiber suspension measured as zeta potential value becomes less negative when bleached softwood pulp is xylanase-treated before refining. A similar change in zeta potential value, but to a greater extent, was observed in this study when xylanase treatment was applied after refining for bleached birch pulp. In addition, the rapid change in the zeta potential value determined for the fiber suspension was seen after as little as 10 minutes of xylanase treatment, as the zeta potential value became less negative by increasing from -81.0 to -64.2 mV. The 4-*O*-methylglucuronic acid side groups bound to the xylan backbone are known to substantially increase the anionic charge of bleached birch kraft pulp fibers (Sjöström 1989). The amount of glucuronic acid released was 21.6 mg/L after 10 minutes of xylanase treatment and, thus, the decreasing fiber charge could be attributed to the removal of the anionic side groups present in the surface xylan of the fiber and fines. This finding further demonstrated that the xylanase solution used has a high hydrolytic activity on GX found in hardwoods. A difference in zeta potential was seen to a lesser extent between the R and XT pulp. This was, however, expected since the R pulp was refined to the same °SR as the XT pulp.

Table XVI Effect of xylanase treatment time on fiber properties. Standard deviations given in brackets.

Fiber property	0 min	10 min	20 min	30 min	60 min	90 min	XT pulp	R pulp
Drainability, °SR	24	-	-	-	-	17	17	17
WRV, %	212	-	-	-	-	195	191	195
Fiber length, mm	0.976	0.926	0.946	0.937	0.938	0.934	0.939	0.976
Fiber width, µm	20.8	20.9	20.8	21.0	20.8	20.9	20.9	20.5
Kink index, 1/m	1300	1460	1610	1620	1670	1690	1690	1280
Zeta potential, mV	-81.0 (0.5)	-64.2 (1.4)	-62.2 (0.3)	-63.8 (0.6)	-61.5 (0.1)	-61.3 (0.1)	-60.5 (0.3)	-64.0 (0.4)
WZST strength, Nm/g	103	-	-	-	-	96	100	107

The concomitant deterioration of fiber strength properties has often been observed with cellulase treatment of pulps (Kibblewhite and Clark 1996; Oksanen et al. 1997a). Oksanen et al. (1997b) have reported that removal of 30% of the original amount of pulp xylan with hemicellulase enzymes has no negative effect on the strength properties of non-refined never-dried bleached birch kraft pulp fibers. In this study, it was demonstrated that, with short xylanase treatment times, the effect on the mechanical properties (such as in-plane tensile and out-of-plane tear) of paper is negligible (Table XVII). However, there was only a slight reduction in the wet zero-span tensile (WZST) strength due to xylanase treatment. The WZST strength gives an indication of the maximum possible tensile strength of the randomly oriented fiber network that can be developed under optimal fiber-to-fiber bonding (Bronkhorst and Bennett 2002b). It thus appeared that surface xylan removal from refined never-dried kraft pulp fibers by means of xylanase does not deteriorate the papermaking properties of the pulp and the strength expectation of the produced paper is at an acceptable level with the xylanase treatment applied in this study.

Table XVII Effect of xylanase treatment time on mechanical paper properties. Standard deviations given in brackets.

Paper property	0 min	10 min	20 min	30 min	60 min	90 min	XT pulp	R pulp
Bulk, cm ³ /g	1.62	1.53	1.59	1.54	1.56	1.57	1.50	1.53
Tensile index, Nm/g	52.7 (2.0)	51.3 (1.4)	48.7 (2.3)	49.9 (2.4)	46.4 (1.6)	46.3 (3.0)	48.4 (1.7)	49.3 (2.8)
Stretch, %	4.1 (0.3)	3.8 (0.4)	4.1 (0.2)	3.9 (0.3)	3.7 (0.3)	3.5 (0.4)	3.8 (0.3)	3.8 (0.2)
TEA index, J/g	1.47 (0.17)	1.47 (0.16)	1.48 (0.11)	1.46 (0.18)	1.31 (0.16)	1.23 (0.21)	1.39 (0.13)	1.46 (0.13)
Tensile stiffness index, kNm/g	6.4 (0.2)	6.3 (0.4)	6.0 (0.3)	6.2 (0.3)	6.0 (0.3)	6.1 (0.3)	6.1 (0.2)	5.8 (0.1)
Tear index, mNm ² /g	7.6 (0.6)	7.9 (0.3)	7.4 (0.5)	8.2 (0.4)	7.0 (0.3)	8.2 (0.6)	8.0 (0.6)	7.3 (0.1)

5.3.3 Papermaking in a pilot-scale environment

The pulp obtained after 90-minute xylanase treatment was used as a raw material for papermaking. The mechanical properties of the 180 g/m² paper made from the XT pulp remained on a similar level compared to the paper made from the R pulp, despite the 14.2% reduction in the total amount of xylan for the XT pulp used (Table XVIII). The greatest differences were observed in bulk, paper stretch, and two-point bending stiffness. Lyttikäinen et al. (2014) demonstrated that reducing the xylan content in birch kraft pulp by means of alkaline extraction has a positive effect on the retention of papermaking chemicals. Thus, it should be pointed out that the process chemical doses were not changed during the trial and therefore the electrostatic charge of both the fibers and the process waters might differ between the studied pulps. This would lead to altered chemical (e.g., starch and alkyl ketene dimer) retention in papers made from R or XT pulp. Thus, also in this case, the results on the determined properties of the paper made from XT pulp were a combination of both the altered hemicellulose content of the pulp and presumably improved paper chemical retention.

Table XVIII Properties of the papers produced in pilot-scale. Values are geometric MD/CD means for strength properties and top/bottom side mean values for other tabulated properties. Standard deviations given in brackets.

TEST POINT	R pulp		XT pulp	
Xylan content, %	24.9	24.9	21.3	21.3
Paper moisture, %	8	8	8	8
Calendering pressure, kN/m	0	20	0	20
Initial wet web strength index, Nm/g	1.90		1.88	
Grammage, g/m ²	190.5	187.3	183.3	185.7
Bulking thickness, μm	236.3 (1.2)	218.9 (0.4)	221.7 (0.6)	209.5 (0.4)
Apparent density, kg/m ³	805	855	825	885
Bulk, cm ³ /g	1.24	1.17	1.21	1.13
Bendtsen air permeance, $\mu\text{m}/\text{Pa s}$	5.9 (0.3)	4.8 (0.2)	4.4 (0.3)	3.7 (0.1)
Bendtsen roughness, mL/min	1390 (97)	600 (99)	1440 (122)	520 (67)
Tensile index, Nm/g	60.9 (2.2)	62.8 (1.9)	60.1 (2.1)	63.8 (2.3)
Stretch, %	3.7 (0.3)	3.3 (0.2)	4.0 (0.2)	3.5 (0.3)
TEA index, J/g	1.59 (0.16)	1.43 (0.14)	1.72 (0.15)	1.61 (0.18)
Tensile stiffness index, kNm/g	6.5 (0.1)	6.9 (0.1)	6.6 (0.2)	7.0 (0.2)
Tear index, mNm ² /g	9.0 (0.4)	9.0 (0.4)	9.2 (0.3)	9.0 (0.4)
Bending stiffness, mNm	24.4 (1.8)	19.1 (0.4)	18.0 (1.5)	18.7 (0.0)
Cobb ₆₀ , g/m ²	24.9	23.7	23.9	23.4

5.4 Evaluation of the hemicellulose extraction concepts

The hemicellulose extraction concept plays a key role in the production of the hemicellulose-extracted fiber stream. In addition, the composition and potential applications of the extracted co-product streams are influenced by the mode of the partial removal of wood hemicelluloses.

5.4.1 Pretreatments prior to kraft pulping

In the pretreatment of softwood chips prior to cooking, the hemicelluloses were recovered as one component of the prehydrolysate and the residual wood material after hemicellulose extraction was used in a conventional kraft pulping process. Pretreatment of softwood chips prior to kraft pulping by a hot-water or dilute-acid prehydrolysis process resulted in a decreased yield on wood after cooking. The dilute-acid catalyzed prehydrolysis process

increased the rate of dissolution of material during prehydrolysis, yet decreased the yield on wood after cooking even further compared to the hot-water prehydrolysis-kraft process. With the hot-water and dilute-acid prehydrolysis-kraft processes, the reduction in the total content of hemicelluloses in the bleached kraft pulp was 45% and 65%, respectively, compared to the unhydrolyzed reference pulp. The lower total amount of hemicelluloses in these prehydrolysis-kraft pulps made them more susceptible to fiber damage in the fiberline processes compared to the unhydrolyzed reference pulp, measured as differences in the morphological character of the non-refined fibers. Furthermore, it appeared that the never-dried prehydrolysis-kraft pulp fibers had fiber-water interaction behavior similar to that of the once-dried and rewetted reference kraft pulp fibers. However, pretreatment of the softwood chips with an alkaline solution prior to cooking had no effects on the yield on wood after cooking and resulted in a 3% reduction in the total hemicellulose content in the bleached kraft pulp compared to the unhydrolyzed reference pulp. Furthermore, no changes in the morphological character of the fiber or fiber-water interaction behavior were observed.

The strength properties of all the non-refined pretreated pulps were lower than those of the reference pulps. Thus, a softwood chip pretreatment for partial removal of hemicelluloses prior to cooking, whether acidic or alkaline, had an impact on the physical properties of non-refined bleached pulp. In addition, all the pretreated pulps exhibited a slower beating response than the unhydrolyzed reference pulp. It is therefore postulated that the physico-chemical changes of the fibers taking place during wood chip pretreatment and subsequent kraft process contribute to the losses in the beating response of pretreated pulps together with the hemicellulose content. With the exception of dilute-acid prehydrolysis-kraft pulp, the papermaking properties of the pretreated pulps were preserved as a function of sheet density when compared to the unhydrolyzed reference pulp. However, the rather significant reduction in the beating response and strength development might present severe problems in the utilization of prehydrolyzed and alkaline pretreated pulps for traditional papermaking purposes.

5.4.2 Alkaline-extracted birch kraft pulp

In the alkaline extraction of bleached birch kraft pulp, the main hemicellulose, xylan in this case, was recovered as a component of the alkaline pulp washing filtrates and the alkaline-extracted pulp was used as a papermaking fiber. The alkaline extraction of bleached birch kraft pulp had direct effects on pulp yield proportionally to the amount of extracted

hemicelluloses, i.e., xylan. It was shown that extraction time had no effect on xylan removal rate and quantity: a similar amount was extracted in 5 minutes as in 60 minutes with 0.56 M NaOH. In fact, the alkali concentration was the only critical parameter in the quantity of xylan removed in the alkaline extraction of bleached birch kraft pulp. The shorter extraction time could simplify the process extraction arrangements significantly. Therefore, the alkaline extraction of xylan from bleached birch kraft pulp could be implemented on an industrial scale if, at a certain alkali concentration, a short extraction time was sufficient to remove the extractable xylan.

The alkaline-extracted birch kraft pulp had a higher swelling tendency and water holding capacity measured as the water retention value of the pulp than the non-extracted reference pulp. This was somewhat surprising, given the fact that the extracted xylan has a distinctly hydrophilic nature. Thus, it seemed that for alkaline-extracted birch kraft pulp, the fiber-water interactions are dictated by a combination of the total hemicellulose content in the pulp together with the ionic forms of the hemicelluloses, which can be converted to their sodium form due to alkaline extraction. Though the swelling of the alkaline-extracted pulp was improved, it had a slower beating response than the non-extracted reference pulp. Investigations made in a pilot-scale papermaking environment revealed that some amount of alkaline-extracted birch kraft pulp, with a 24.9% reduction in the total amount of xylan, could be used in the papermaking stock as a mixture with non-extracted pulp without affecting the mechanical properties of the 75 g/m² paper produced. In particular, with a ratio of 25 to 75 of alkaline-extracted to non-extracted pulp, the mechanical properties of the produced paper were unaffected.

5.4.3 Xylanase-treated birch kraft pulp

In the xylanase treatment of bleached birch kraft pulp, the main hemicellulose, xylan in this case, was recovered as xylose and xylooligomer units in the pulp washing filtrates and the xylanase-treated pulp was used as a papermaking fiber. Xylanase treatment of birch kraft pulp indicated very surface-selective xylan removal from the fibers and had direct effects on pulp yield in proportion to the amount of hydrolyzed xylan. The water holding capacity of the pulp measured as the water retention value decreased as a result of the xylanase treatment. For xylanase-treated fibers this could be attributed to the removal of surface xylan from the fiber and fines. This finding on fiber-water interaction behavior further emphasized the effect of the hemicellulose removal method from bleached birch kraft pulp on the resultant pulp properties.

The concomitant deterioration of the papermaking properties of the fibers due to the xylanase treatment was minor, which enabled the use of xylanase-treated fibers in papermaking. Investigations made in a pilot-scale papermaking environment revealed that the properties of 180 g/m² paper made from xylanase-treated fibers remained similar to paper made from the reference birch pulp. However, there was a 14.2% reduction in the total amount of xylan in the xylanase-treated pulp compared to the reference pulp.

The main effects of the studied hemicellulose extraction concepts on the process, pulp, and paper properties are shown in Table XIX.

Table XIX Summary of the effects of various hemicellulose removal methods on the pulping process, pulp quality, and the obtained co-product streams.

1. Pretreatments prior to kraft pulping	
<i>Process and pulp properties</i>	<i>Co-product</i>
<ul style="list-style-type: none"> - Can affect the cooking yield - Interconnected to the fiberline - effects on pulping processes (cooking and bleaching) - Fiber morphology and fiber-water interactions are changed - Decreased strength properties of non-refined pulp - With optimal pretreatment the papermaking properties of refined pulp stay on a similar level to the reference pulp 	<ul style="list-style-type: none"> - Heterogeneous prehydrolysate mixture
2. Alkaline extraction of bleached kraft pulp	
<i>Process and pulp properties</i>	<i>Co-product</i>
<ul style="list-style-type: none"> - Direct effects on pulp yield - Can be a separate process - NaOH circulation could presumably be integrated to the pulp mill line - Short extraction times - Very selective carbohydrate component removal - Some amount of alkaline-extracted BBKP could be used in PM stock without losing paper mechanical properties 	<ul style="list-style-type: none"> - Xylan, polymeric and pure
3. Enzymatic (xylanase) treatment of bleached kraft pulp	
<i>Process and pulp properties</i>	<i>Co-product</i>
<ul style="list-style-type: none"> - Direct effects on pulp yield - Can be a separate process - Highly selective and surface-specific carbohydrate component removal - Properties of both laboratory (60 g/m²) and pilot-scale produced paper (180 g/m²) were similar to paper made from the reference pulp 	<ul style="list-style-type: none"> - Enzymatic hydrolysis products (monomers and oligomers)

6 CONCLUDING REMARKS

The purpose was to clarify the effect of various hemicellulose extraction processes for partial removal of hemicelluloses from wood and pulp material on the properties of paper-grade kraft pulp fibers. When comparing the various hemicellulose extraction methods, it was evident that the hemicellulose content in pulp alone does not explain the changes in fiber and paper properties, since morphological, chemical, and physical changes occurring during and after the hemicellulose extraction process also have an influence. Consequently, the investigated hemicellulose extraction processes contribute to the implementation of the hemicellulose extraction concept in an integrated forest biorefinery.

This study revealed differences in the physico-chemical properties between hemicellulose-extracted pulps together with the chemical composition and quantity of the co-product streams, depending on the method for partial removal of hemicelluloses. Furthermore, effects on the pulp yield were observed with all of the hemicellulose extraction concepts examined. Thus, the value from the hemicellulose co-product stream should compensate any possible losses in pulp yield in order to obtain an economically viable process. The hemicellulose extraction concept should aim to upgrade the value of the fibers for their end use by simultaneously offering additional revenues for the mill from the extracted co-product stream. For these reasons, hemicellulose-extracted pulp is not likely to be a bulk product, but a specialty fiber with smaller volumes and high price intended for selected end-use applications. Hence, the *economies of scope* mentality related to forest biorefining operations should be realized to develop sustainable competitive advantage based on the examined hemicellulose extraction concepts.

This research focused on the characteristic properties of papermaking fibers with decreased hemicellulose content prepared by alternative hemicellulose removal processes for partial removal of hemicellulose from wood and kraft pulp. The results obtained have increased the knowledge on the opportunities of utilizing these kinds of hemicellulose-extracted fibers for traditional papermaking purposes or as a functional fiber in novel applications. The observations reported in this work could generate new ideas on how to interlink hemicellulose extraction processes in an existing fiberline or an integrated pulp and paper mill to produce fibers with targeted physico-chemical properties in conjunction with a valuable co-product stream.

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APPENDIX I

Table I Bleaching chemical dosages and consumptions in the (O)DED bleaching sequences and the development of ISO brightness and pulp viscosity in the bleaching of Groups 1 and 2 pulps.

	Group 1			Group 2			
	Pulp 1	Pulp 2	Pulp 3	Ref	PHW	AcidH	AlkE
Kappa number	25.4	24.4	33.1	25.4	27.7	27.2	27.3
Brightness, %	Not determined			31.2	29.9	32.1	33.0
Viscosity, mL/g	1280	1320	1280	1230	1330	1140	1260
Total yield % on wood	49.5	42.3	42.8	47.0	42.1	39.5	46.9
O₂ delignification							
NaOH charge, %	2.0	2.0	2.0	1.45	1.35	1.21	1.7
ISO brightness, %	37.7	42.5	39.4	33.9	34.1	36.2	33.6
Kappa number	16.1	13.6	16.4	15.3	15.1	13.4	15.6
Kappa reduction, %	36.6	44.3	50.5	39.8	45.5	50.7	42.9
Viscosity, mL/g	1055	1070	1010	1080	1100	1010	1060
Yield, %	98.0	98.1	97.2	98.5	97.95	97.77	97.96
Yield on wood, %	48.5	41.5	41.6	46.3	41.2	38.6	46.0
D₀ stage							
ClO ₂ charge, % act.Cl	3.22	2.72	3.28	3.67	3.62	3.22	3.74
ClO ₂ consumed, % act.Cl	3.22	2.72	3.28	3.67	3.62	3.22	3.74
Final pH (slurry at 50°)	1.9	1.7	1.7	2.2	2.1	2.2	2.1
E₁ stage							
NaOH charge, %	1.93	1.63	1.97	1.29	1.27	1.13	1.31
Final pH (slurry at 60°)	12.6	12.5	12.6	10.8	10.7	10.7	10.8
ISO brightness, %	54.7	58.1	56.2	59.9	60.3	64.3	61.4
Kappa number	3.7	3.3	3.5	3.3	2.9	2.3	3.0
D₁ stage							
ClO ₂ charge, % act.Cl	1.00	1.00	1.00	2.75	2.45	2.01	2.38
ClO ₂ consumed, % act.Cl	1.00	1.00	1.00	2.35	2.13	1.71	2.16
Final pH (slurry at 70°)	3.6	3.8	3.7	3.1	3.1	3.2	3.2
ISO brightness, %	74.1	73.7	71.9	87.6	87.1	87.8	87.6
Kappa number	Not determined			0.8	0.7	0.6	1.0
Viscosity, mL/g	998	990	935	970	960	900	990
Bleaching yield, %	96.5	97.4	96.9	97.0	97.3	96.9	96.8
Consumption of ClO ₂ , calculated as total act. chlorine (kg Cl per tonne of pulp)	42.2	37.2	42.8	60.2	57.5	49.3	59.0
Bleachability*, Unit Kappa/kg Cl	0.38	0.37	0.38	0.25	0.26	0.27	0.26

*calculated as kappa number after O₂-stage divided by the total active chlorine consumption in bleaching. The higher the number, the higher is the bleachability.

APPENDIX I

Table II Content of selected metals and hexenuronic acid in the brown stock of Group 2 pulps, i.e., pulp prior to the O₂ delignification stage

	Ref	PHW	AcidH	AlkE
Hexenuronic acid, mmol/kg	31	11	11	30
Hexenuronic acid, mg/100mg	0.54	0.20	0.19	0.53
Fe, mg/kg	9.6	5.2	4.7	7.0
Cu, mg/kg	0.9	0.3	0.2	0.2
Mn, mg/kg	53	21	11	46
Ca, mg/kg	500	490	160	300
Mg, mg/kg	150	64	37	150
Ni, mg/kg	0.4	0.2	0.1	0.1

APPENDIX II

Table I Properties of base paper and surface-sized paper made from five mixtures of non-extracted and alkaline-extracted pulp. Properties are geometric MD/CD means for strength properties and top/bottom side mean values for other tabulated properties.

Property	Calendering, kN/m	0:100	25:75	50:50	75:25	100:0
General properties						
Grammage, g/m ²	0*	77.8	76.5	75.5	77.6	76.1
	0	78.3	77.4	x	x	78.4
	15	80.9	76.9	x	x	78.2
	30	80.7	75.7	76.6	x	77.8
Bulking thickness, µm	0*	121	122	127	125	119
	0	122	120	x	x	125
	15	116	112	x	x	115
	30	113	108	109	x	109
Apparent bulk density, kg/m ³	0*	643	627	594	621	639
	0	642	645	x	x	627
	15	697	687	x	x	680
	30	714	701	703	x	714
Bulk, cm ³ /g	0*	1.56	1.59	1.68	1.61	1.56
	0	1.56	1.55	x	x	1.59
	15	1.43	1.46	x	x	1.47
	30	1.40	1.43	1.42	x	1.40
Ash content, %	0*	19.7	20.7	21.1	21.0	21.6
	0	19.9	20.3	-	-	20.8
	15	-	-	-	-	-
	30	-	-	-	-	-
Structural and topographical properties						
Air resistance Gurley, s	0*	6	6	6	6	5
	0	6	6	x	x	5
	15	7	6	x	x	6
	30	7	6	6	x	6
Bendtsen roughness, mL/min	0*	594	608	768	829	575
	0	661	668	x	x	681
	15	373	355	x	x	354
	30	265	275	235	x	238
PPS 0.5, µm	0*	6.37	6.34	6.47	6.52	6.35
	0	6.45	6.44	x	x	6.44
	15	6.22	6.18	x	x	6.18
	30	6.04	6.04	5.97	x	5.93
PPS 1.0, µm	0*	6.09	6.06	6.27	6.33	6.06
	0	6.25	6.25	x	x	6.24
	15	5.98	5.92	x	x	5.90
	30	5.71	5.72	5.64	x	5.59
PPS 2.0, µm	0*	5.57	5.55	5.80	5.88	5.54
	0	5.84	5.83	x	x	5.80
	15	5.54	5.47	x	x	5.46
	30	5.23	5.25	5.17	x	5.13

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Optical properties						
Gloss, %	0*	5.09	4.94	4.39	4.14	4.59
	0	5.09	4.99	x	x	4.64
	15	5.69	5.54	x	x	5.28
	30	6.29	5.99	6.14	x	5.79
Brightness D65/10°, %	0*	88.2	88.2	88.3	88.4	88.2
	0	87.5	87.4	x	x	87.7
	15	87.7	87.4	x	x	87.7
	30	87.6	87.5	87.8	x	87.7
Brightness C/2°, %	0*	87.8	87.8	87.9	88.0	87.8
	0	87.1	87.0	x	x	87.2
	15	87.3	87.1	x	x	87.3
	30	87.3	87.2	87.3	x	87.3
Opacity C/2°, %	0*	87.8	87.7	88.2	88.4	88.5
	0	87.0	86.8	x	x	88.0
	15	87.1	86.9	x	x	87.8
	30	87.1	86.6	87.3	x	87.9
Light adsorption co-efficient, m ² /kg	0*	0.200	0.200	0.204	0.200	0.214
	0	0.200	0.200	x	x	0.220
	15	0.190	0.200	x	x	0.215
	30	0.190	0.200	0.210	x	0.220
Light scattering co- efficient, m ² /kg	0*	57.43	58.19	61.13	60.44	61.19
	0	53.07	53.19	x	x	56.39
	15	52.27	54.04	x	x	56.14
	30	52.23	54.03	55.42	x	56.83
Strength properties						
Strain at break, %	0*	2.09	2.07	2.14	2.50	2.22
	0	2.70	2.81	x	x	2.77
	15	2.75	2.76	x	x	2.81
	30	2.53	2.62	2.64	x	2.78
Tensile index, Nm/g	0*	24.8	24.0	25.2	23.8	22.0
	0	41.3	38.8	x	x	34.5
	15	41.9	39.6	x	x	35.2
	30	40.0	38.5	36.8	x	34.5
Tensile stiffness index, kNm/g	0*	4.32	4.08	4.11	3.36	3.38
	0	5.48	4.86	x	x	4.41
	15	5.39	4.85	x	x	4.26
	30	5.24	4.80	4.38	x	4.15
Elastic modulus, MPa	0*	2778	2559	2443	2088	2163
	0	3517	3134	x	x	2766
	15	3758	3327	x	x	2896
	30	3743	3363	3081	x	2963
TEA index, J/g	0*	0.403	0.388	0.427	0.498	0.413
	0	0.809	0.815	x	x	0.739
	15	0.828	0.803	x	x	0.763
	30	0.718	0.774	0.720	x	0.737
Tear index, mNm ² /g	0*	5.47	5.24	5.48	5.59	5.16
	0	6.75	6.43	x	x	6.56
	15	6.71	6.34	x	x	6.46
	30	6.60	6.29	6.51	x	6.11

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Burst index, kPam ² /g	0*	12.0	11.4	12.1	12.6	10.5
	0	21.2	20.6	x	x	19.2
	15	22.7	20.1	x	x	18.9
	30	21.5	20.0	20.1	x	18.8

x = no samples for testing due to web breaks.

* = base paper.

APPENDIX III

In order to verify the surface-specific effect of the endo-1,4- β -xylanase (Shearzyme 500 L) used in Paper IV, a theoretical calculation was made of how much xylan is located in the outer surface layers of kraft pulp fibers. Viikari et al. (1994b) and Teleman et al. (2001) have reported that xylanase is active mainly on the pulp surface and on the accessible surface macropores in the fiber cell wall. Thus, it is assumed that the xylanase treatment was very surface-specific and the xylan dissolved from the fibers originated from the surface layer (primary wall P and outer secondary cell wall layer S_1) of the fibers.

The theoretical value for surface xylan content was calculated based on the following assumptions and measurements:

1. The cell wall layer thickness values for the primary cell wall (P) and outer secondary cell wall layer (S_1) of the fiber surface layers used in the calculations were taken from the literature (Harada 1965; Sjöström 1993; Bergander and Salmén 2002). The general structure of a wood fiber, typical thickness levels, and cellulosic microfibril angles (MFAs) of the cell wall layers are illustrated in Figure 1.

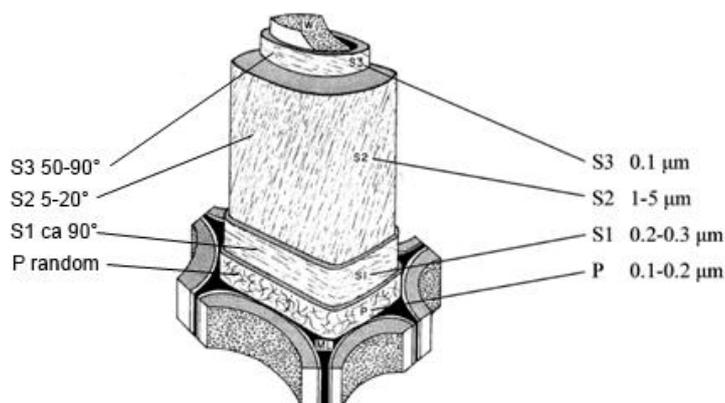


Figure 1 Fiber model showing cell wall layers, their thickness levels, and cellulosic microfibril angle (MFA), modified from Sjöberg (2003). MFAs according to Donaldson (2008).

2. Fiber width, cell wall thickness (CWT), and lumen width values of ECF-bleached non-refined never-dried birch kraft pulp prior to xylanase treatment were measured with an optical fiber analyzer (Kajaani FiberLab, Metso Automation).
 - a. Prior to the xylanase treatment, the pulp was refined to °SR 24. However, the P/ S_1 layer is known to be fibrillated and some parts of the outer layers of the fibers can be detached from the fiber surface, generating ‘*secondary fines*’ (see e.g., Ebeling 1980; Page 1989). Furthermore, external fibrillation and fines generation during refining is known to affect the cell wall swelling properties of the fiber (Ebeling 1980; Page 1989). Therefore, values for non-refined pulp were used in the calculations.
3. The concentration of xylan on the surface layers of hardwood fibers, i.e., 40%, was taken from the literature.
 - a. “It has been stated that for bleached hardwood kraft fibers the surface xylan concentration can be as high as 40%” (Dahlman et al. 2003; Sjöberg 2003).
4. The value for the xylan content in the whole cell wall (primary wall P and secondary cell wall layers S_1 , S_2 , and S_3) in the studied ECF-bleached never-dried birch kraft pulp was 24.9%.

APPENDIX III

- a. After the 90-minute xylanase treatment used in this study, 3.6% of the original pulp dry weight was hydrolyzed, with the majority (96.7%) of the xylose derived from the β -1,4-backbone of xylan (see Table XV in Chapter 5.3.1). Together with the 0.5% rhamnose and 1.7% glucuronic acid in the pulp filtrates, the amount of xylan-derived compounds can be estimated to be over 98.5% after 90 minutes of xylanase treatment.
- b. This amount of removed xylan corresponds to 14.2% of the total amount of xylan, calculated from the 24.9% xylan content in pulp.
 - i. $\text{Xylan amount removed, \%} = (3.6\% \times 0.985 \div 24.9\%) \times 100\% \approx 14.2\%$

Calculations

The layer thickness for the outer cell wall layers ($P + S_1$) was assumed to be the average of 0.3-0.5 μm , i.e., 0.4 μm . It was assumed that the fibers are perfectly uniform, cylinder-like particles (Figure 2) and thus the xylan content can be calculated from the cross-section of a fiber as a cross-sectional area (CSA).

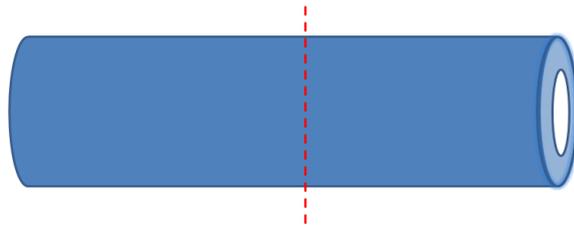


Figure 2 An illustration of the shape of the fibers used in the calculations. Fibers are presented as cylinder-like particles having a uniform xylan distribution in the longitudinal direction of the fibers with a hollow interior representing the lumen.

The calculations were made based on the above-mentioned assumptions, which are illustrated in Figure 3.

APPENDIX III

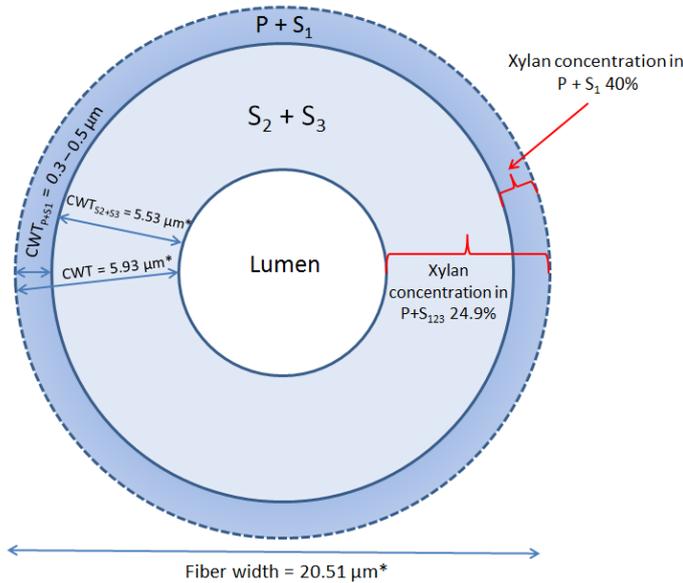


Figure 3 Cross-section of a fiber and the values for cell wall layer thicknesses and xylan concentrations used in the calculations. * = values measured with an optical fiber analyzer.

The cross-sectional area (CSA_{Whole}) of the fiber:

- Cross-sectional area of the fiber $CSA = \text{Annulus}$, which is equivalent to the measured fiber width W and fiber wall thickness CWT
 - $CSA_{Whole} = \pi \cdot CWT (W - CWT)$
- $CSA_{whole} = \pi \times 5.93 \mu m (20.51 \mu m - 5.93 \mu m) = 271.62 \mu m^2$

The cross-sectional area of the secondary cell wall layers S_2 and S_3 (CSA_{S2+S3}) of the fiber:

- $CSA_{S2+S3} = \pi \cdot CWT_{S2+S3} \cdot (W - CWT_{S2+S3} - 2 \cdot P/S_1 \text{ layer thickness})$
- If the outer cell wall layer (P/S_1) is $0.4 \mu m$ thick:
 - $CSA_{S2+S3} = \pi \times 5.53 \mu m (20.5 \mu m - 5.53 \mu m - 2 \times 0.4 \mu m) = 246.35 \mu m^2$

The cross-sectional area of the outer cell wall layers P and S_1 (CSA_{P+S1}) of the fiber:

- $CSA_{P+S1} = CSA_{Whole} - CSA_{S2+S3}$
- If the outer cell wall layer (P/S_1) is $0.4 \mu m$ thick:
 - $CSA_{P+S1} = 271.62 \mu m^2 - 246.35 \mu m^2 = 25.27 \mu m^2$

The concentration of xylan on the outer cell wall layers P and S_1 (CSA_{P+S1}) of the fiber is 40%. Thus, xylan covers the following area in the outer ($P + S_1$) layer of the cell wall (μm^2):

- $A_{xylan \text{ on surface}} = CSA_{P+S1} \cdot 0.4$
 - $A_{xylan \text{ on surface}} = 25.27 \mu m^2 \times 0.4 = 10.11 \mu m^2$

The concentration of xylan in all the cell wall layers ($P + S_{123}$) of the fiber is 24.9%. Thus, xylan covers the following area in the whole ($P + S_{123}$) cell wall (μm^2):

- $A_{xylan \text{ in the whole cell wall}} = CSA_{Whole} \cdot 0.249$
 - $A_{xylan \text{ in the whole cell wall}} = 271.62 \mu m^2 \times 0.249 = 67.63 \mu m^2$

APPENDIX III

Therefore, the amount of xylan that is on the outer layer (P + S₁) of the fiber is:

- $Xylan - \%_{P+S_{123}} = (A_{xylan \text{ on surface}} / A_{xylan \text{ in the whole cell wall}}) \cdot 100\%$
 - $Xylan \%_{P+S_{123}} = (10.11 \mu m^2 \div 67.63 \mu m^2) \times 100\% \approx 14.9\%$

The amount of xylan that was removed from the fibers in this study was 14.2% and the theoretical value of xylan on the surface layers (P + S₁) of 14.9% (Figure 4) indicates that virtually all the surface xylan was removed. This further verifies that the xylan removed from the fibers originates from the surface layer and from the accessible surface macropores in the fiber cell wall.

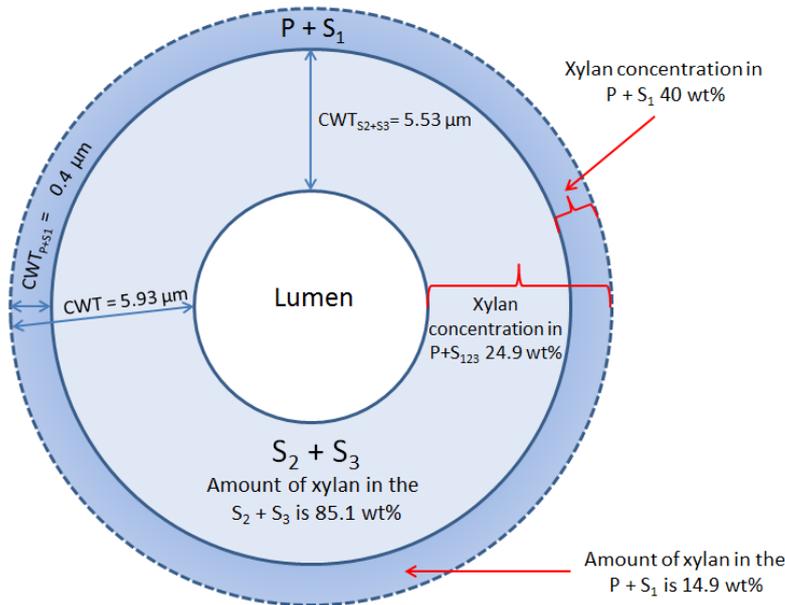


Figure 4 Theoretically evaluated amounts of xylan (%) in the outermost surface layer (primary wall P and outer secondary cell wall layer S₁) and secondary cell wall layers S₂ and S₃. The CWT_{P+S₁} value of 0.4 μm is according to Harada (1965), Sjöström (1993), and Bergander and Salmén (2002). The CWT value was determined with an optical fiber analyzer. The concentration of xylan in the surface layer (P+S₁) is 40%, according to Dahlman et al. (2003) and Sjöberg (2003). The content of xylan in the whole cell wall (P+S₁₂₃) for the ECF-bleached birch kraft pulp used in this study was 24.9%.

PUBLICATION I

Digestibility and paper-making properties of prehydrolyzed softwood chips

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DIGESTIBILITY AND PAPER-MAKING PROPERTIES OF PREHYDROLYZED SOFTWOOD CHIPS

Jesse Kautto,^{a*} Esa Saukkonen,^b and Kaj Henricson^b

The effect of hemicellulose extraction of pine wood chips by water prehydrolysis on subsequent kraft cooking and paper properties was studied. Prehydrolysis reduced the required cooking time by approximately 40% and increased kappa number reduction in oxygen delignification. Prehydrolysis decreased the overall brownstock pulp yield on wood by 7.2 percentage units. Consequently, valuable products would need to be produced from the prehydrolyzate to compensate for the resulting increase in wood consumption. In DED-bleaching, lower bleaching chemical dosages were needed with prehydrolyzed than with unhydrolyzed pulps to obtain similar final brightness. As expected, removal of hemicelluloses led to a decrease in the tensile index and increase in the tear index. At a given density, the strength potential of prehydrolyzed pulps was higher than that of unhydrolyzed pulps. There was an up to more than fivefold increase in beating revolutions in a PFI-mill needed to obtain comparable tensile indices. This significant reduction in beating response might pose problems in the commercialization of prehydrolyzed pulps. In general, differences between the paper properties of prehydrolyzed pulps and unhydrolyzed pulps are attributed to decreased inter-fiber bonding in prehydrolyzed pulps.

Keywords: Water prehydrolysis; Cooking; Bleaching; Beating; Paper-making properties

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INTRODUCTION

The finite nature of fossil fuels and their contribution to carbon dioxide emissions have motivated increasing interest in biofuels. This, in turn, has led to the development of various biorefinery concepts (see, e.g. Kamm and Kamm 2004) in which biomass is converted to biomaterials and biofuels in fully integrated systems. Existing forest industry facilities could play a key role in the utilization of lignocellulosic biomass, as the people who run such facilities already possess the know-how, logistics, and infrastructure for procuring, transporting and processing lignocellulosics. Thus, different biorefinery concepts aimed at combining biofuel production with pulp and paper production have attracted interest in academia and industry. These concepts can be called, e.g., integrated forest biorefineries (IFBR) (van Heiningen 2006).

One option to convert a pulp mill into a pulp and biofuels and/or biochemicals producing biorefinery would involve the extraction of hemicelluloses from wood chips. As a steam-phase prehydrolysis process, hemicellulose extraction is conventionally used in the production of high-purity dissolving pulps. Carried out in an aqueous phase, hemicellulose extraction could enable the extraction of valuable hemicelluloses prior to kraft paper pulp production. Hydrolyzation of hemicelluloses

to monomeric sugars with fermentation to ethanol would enable the co-production of ethanol and pulp. An existing pulp mill in Old Town, Maine, USA, is currently being converted to a biorefinery utilizing hemicellulose extraction technology (Pendse *et al.* 2009). In addition to ethanol, other products and chemicals could also be produced from hemicelluloses, such as films and coatings (Hansen and Plackett 2008). The sugars formed in the hydrolysis of hemicelluloses could be used to produce various chemicals; a U.S. DOE study lists over 300 potential building block chemicals that could be produced from sugars and synthesis gas of biomass (Werpy *et al.* 2004).

The extraction of hemicelluloses from wood chips can be done prior to cooking in a so-called pre-extraction process. Several methods for the extraction of hemicelluloses have been reported. In a prehydrolysis process, the hemicelluloses are hydrolyzed to oligomeric and monomeric sugars with the aid of, for example, pressurized hot water (autohydrolysis) (e.g. Casebier *et al.* 1969; Garrote and Parajo 2002; Yoon *et al.* 2008; Al-Dajani *et al.* 2009; Leschinsky *et al.* 2009), dilute acids (e.g. Parajó *et al.* 1994; Frederick. *et al.* 2008; Al-Dajani *et al.* 2009) or steam (e.g. San Martín *et al.* 1995). Hemicelluloses can also be extracted by alkaline extraction before (e.g. van Heiningen *et al.* 2008; Al-Dajani and Tschirner 2008) or even after pulping (Pekkala 2008).

When commercializing these hemicellulose pre-extraction processes, their effect on the kraft fiber line and on the papermaking properties of subsequent pulps is of key importance. The extraction of hemicelluloses has been reported to affect cooking (Sixta 2006a; Smith *et al.* 2008; Yoon and van Heiningen 2008; Al-Dajani *et al.* 2009), O₂-delignification (Antonsson *et al.* 2003; Sixta 2006b,c), hornification and swelling tendency (Oksanen *et al.* 1997; Moss and Pere 2006), beating response (Vaaler *et al.* 2002; Yoon and van Heiningen 2008), and strength properties (Spiegelberg 1966; Rydholm 1967; Kettunen *et al.* 1982; Molin and Teder 2002). Although several studies on the effect of hemicellulose extraction on various isolated aspects of fiber line and paper-making properties have been published, more comprehensive studies on the pulping and paper making properties of hemicellulose-extracted chips are lacking. Yoon and van Heiningen (2008) have studied the digestibility, beatability, and paper properties of hot-water prehydrolyzed loblolly pine (*Pinus Taeda*) chips. With the exception of Yoon and van Heiningen (2008), there appear to be no studies comprising the whole fiber line, including bleaching and testing of bleached sheets. There is therefore a need for a study examining the whole fiber line, from hemicelluloses extraction and cooking to testing of bleached pulps.

This paper is part of the *Biojalostamo Sellutehdas (BiSe)* project, studying the conversion of a conventional kraft pulp mill into a pulp and biofuel-producing biorefinery. It is continuation to a paper presented elsewhere (Kautto *et al.* 2010) in which the integration of a prehydrolysis bioethanol process to a kraft pulp mill was discussed. This paper discusses the effect of water prehydrolysis of pine wood chips on cooking, oxygen delignification, bleaching, beating, and paper properties.

EXPERIMENTAL

The cooking experiments were carried out in the Department of Forest Products Technology at Aalto University, School of Science and Technology. The pulp beating, bleaching, and papermaking property experiments were carried out at NabLabs Oy, Rauma, Finland.

Materials

The wood raw material used was industrial pulp wood chips collected from a pulp mill located in South-East Finland. The raw material was mainly Scots pine (*Pinus Sylvestris*), and the sample possibly contained some amount of Norway spruce (*Picea Abies*). The industrial wood chips were screened (SCAN-CM 40:01). The accepts were the fraction passing 7 and 13 mm slot sizes. The fraction was then manually checked for knots and bark.

Methods

The experiments were carried out for an unhydrolyzed reference pulp (**pulp 1**) and for prehydrolyzed pulps cooked at sulfidity levels of 40% (**pulp 2**) and 20% (**pulp 3**). The reference pulp 1 was cooked at a sulfidity level of 40% and then bleached. Pulps 2 and 3 were first prehydrolyzed with hot water at 150 °C and then cooked and bleached.

Prehydrolysis at P-factor 200

Pulps 2 and 3 were prehydrolyzed with hot water for the extraction of hemicelluloses. In the prehydrolysis, 3000 g of pine wood chips were placed in a 20 liter digester. Deionized hydrolysis water was then introduced to the digester to obtain a liquor-to-wood ratio of 4.6 L/kg. The mixture was first heated to 80 °C, and then to 150 °C at a rate of 2 °C/min. The mixture was kept at 150 °C for 1 h 33 min. This corresponds to a P-factor of 200. The P-factor is a term representing the severity of a hot water hydrolysis treatment. The P-factor was calculated from the recorded temperature/time data according to Sixta (2006a), based on an activation energy of 125.6 kJ/mol. After the set time, a valve was opened at the bottom of the digester, and the hydrolysis liquor (prehydrolyzate) was drained from the digester. The wood chips were then cooked. There was no intermittent chip washing between prehydrolysis and cooking.

Cooking

The cooking was carried out in the same digester as used in the prehydrolysis. With pulps 2 and 3, the hydrolyzate was drained from the digester after prehydrolysis. With pulp 1, 3000 g of chips were placed in the digester. 1 liter of deionized water was introduced to the digester. The liquid-to-wood ratio was then adjusted to 4.6 by adding deionized water and cooking chemicals. The effective alkali (EA) level during cooking was 20%, expressed as NaOH based on oven dry wood, in all cooks. The sulfidity level was 40% for pulps 1 and 2 and 20% for pulp 3. The digester was first heated to 80 °C, and then to the cooking temperature of 160 °C at a rate of 1.5 °C/min. The cooking was stopped at an H-factor of 1600 in the case of the reference pulp. This H factor corresponded to a cooking time of 3 h 51 min. With pulp 2, the cooking was stopped at an H-factor of 1000 (cooking time of 2 h 22 min), and with pulp 3, the cooking was stopped at an H-factor of 1300 (3 h 6 min). Draining of the digester was started two minutes before the set cooking time. After the set cooking time had been reached and the digester had been drained, the digester was filled with NaOH solution (5 g/L). The mixture was then heated to 80 °C and kept at 80 °C for 10 minutes. It was subsequently drained, and the digester was filled with deionized water. The mixture was similarly heated to 80 °C and kept at 80 °C for 10 minutes. After that, the water was drained and the NaOH solution treatment was repeated two

times. The pulp was then removed from the digester, centrifuged, homogenized, and weighed. Its dry solids content was measured according to SCAN-C 3:78. The metal content of the pulps was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Screening

The pulps were first wet disintegrated and then screened with a TAP031 screener with a 0.25 mm slot size. The accepts fraction was then homogenized. The dry solids content of the accepts and rejects was then analyzed according to SCAN-C 3:78.

Bleaching

All pulps were oxygen delignified and subsequently bleached with a DED-sequence. Oxygen delignification was done for 600 gram pulp batches in a 16 litre rotating pressurized cooking apparatus. The count for the 30-minute reaction time started when the temperature of the cooking apparatus reached 89 °C. After oxygen delignification the pulps were washed three times with 12 litres of deionized water and homogenized for three minutes with a Tripas Planet kitchen mixer.

Unpressurized laboratory bleaching was carried for 300 gram pulp batches in plastic bags in a hot water bath. ClO₂ for the bleaching stage was acquired from a pulp mill located in Western Finland as a water solution. Appropriate safety measures were taken in handling the solution and the D bleaching stage (ventilated hood, safety goggles and mask etc.). Chemical charges used in the bleaching stages D₀ and E were calculated from the kappa number after O₂-delignification. Chemical charge in the D₁-stage was the same for every pulp batch. Pulps were washed two times with 60 litres of deionized water after the D₀- and D₁-stages and a similar procedure plus an additional wash with 20 litres of deionized water was applied after the E-stage. The oxygen delignification and bleaching conditions for all pulps are presented in Table 1.

Table 1. Oxygen Delignification and Bleaching Conditions with Chemical Charge Amounts

Sequence	O	D ₀	E	D ₁
Pulp consistency, %	10	10	10	10
Act. Cl charge %		0.2×incoming kappa		1
NaOH charge %	2		0.6×D ₀ charge	
Temperature, °C	90	60	60	70
Time, min	30	45	75	180
Pressure, bar	5			
Target end pH		~2	~12	~3.6

Viscosity (ISO 5351-1:1981) of the pulp samples was measured after O₂-delignification and bleaching stages E and D₁. The ISO brightness (ISO 2470:1999) of the pulp samples was measured after O₂-delignification and bleaching stages E and D₁. Kappa numbers (ISO 302:2004) were determined before and after oxygen delignification.

Handsheet properties

The mechanical properties of the pulps were evaluated by handsheet testing (ISO 5270:1998). The pulps were refined in a PFI mill (ISO 5264-2:2002), handsheets were prepared (ISO 5269-1:1998) with different degrees of beating, and the CSF-values were measured (ISO 5267-2:2001).

RESULTS AND DISCUSSION**The Effect of Prehydrolysis on Cooking and Oxygen Delignification of Chips**

Prehydrolysis of the wood chips was carried out at P-factor of 200 at 150 °C. For prehydrolyzed pulps 2 and 3 the hydrolyzate was then drained from the digester and the chips were cooked and oxygen delignified. With constant conditions in oxygen delignification, the target kappa number after O₂-delignification was 15 for all pulps. Based on earlier experiments on smaller scale laboratory digesters (presented in Kautto et al. 2010), it was assumed that prehydrolyzed chips can be cooked at lower H-factors and that they respond better to O₂-delignification. The cooking of prehydrolyzed chips was therefore carried out with lower H-factors, and the target kappa numbers after cooking were higher. Pulp 2 was cooked at an H-factor of 1000 at a sulfidity level of 40% and pulp 3 at an H-factor of 1300 at a sulfidity level of 20%. The reference chips (pulp 1) were cooked at an H-factor of 1600. Figure 1 presents the yields on wood and kappa numbers of prehydrolyzed and unhydrolyzed chips after cooking and O₂-delignification. Table 2 presents the yields on wood, kappa numbers, residual alkalis, viscosities, and ISO-brightnesses after cooking and O₂-delignification.

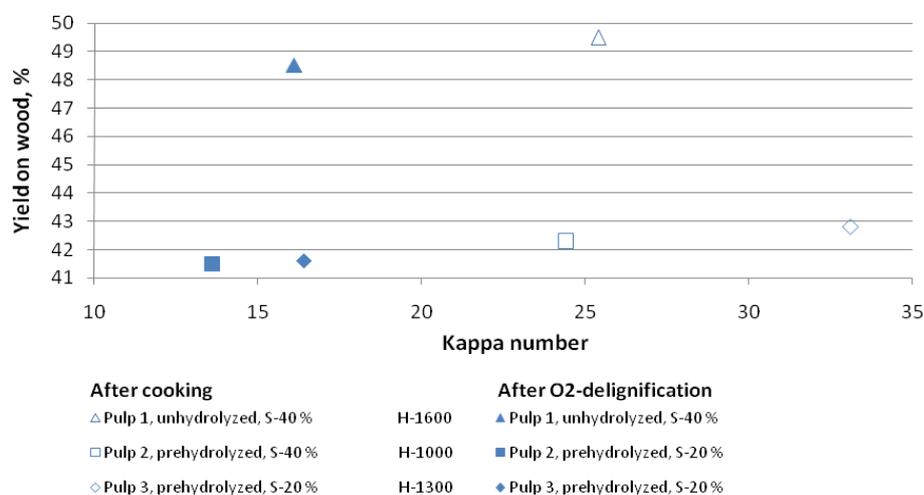


Fig. 1. Yield on wood versus kappa number after cooking and oxygen delignification of pulp 1 (unhydrolyzed reference chips cooked at a sulfidity of 40% at an H-factor of 1600) and pulps 2 and 3 (chips prehydrolyzed at a P-factor of 200 and cooked at an H-factor of 1000 and a sulfidity level of 40%, and at an H-factor of 1300 and a sulfidity level of 20%, respectively). Effective alkali level was 20% in all cooks.

Table 2. Yield on Wood, Kappa, Residual Alkali, and Viscosity after Cooking for Pulps 1, 2, and 3

Pulp	Cooking				O ₂ -delignification			
	Yield on wood, %	Kappa	Residual alkali, g/l	Viscosity, ml/g	Yield on wood, %	Kappa	ISO-brightness	Viscosity, ml/g
1	49.5	25.4	7.9	1280	48.5	16.1	37.7	1055
2	42.3	24.4	9.8	1320	41.5	13.6	42.5	1070
3	42.8	33.1	10.5	1280	41.6	16.4	39.4	1010

As can be seen in Fig. 1, at similar sulfidity levels of 40%, the H-factor can be lower with prehydrolyzed chips to obtain similar kappa numbers. The H-factors for reference and prehydrolyzed chips were 1600 and 1000, and kappa numbers after cooking were 25.4 and 24.4, respectively. With a cooking temperature of 160 °C and a heating rate of 1.5 °C/min, this would be equivalent to a shortening of the cooking time from 3 h 51 min to 2 h 22 min (39%). This is in line with the findings of Yoon and van Heiningen (2008), who report that with approximately 5% to 8% of wood material (loblolly pine) extracted during water prehydrolysis, the delignification rate constants in the subsequent kraft cooking are 40% to 60% higher than with unhydrolyzed chips. The lower required H-factors and higher delignification rates would imply that the digestibility of prehydrolyzed chips is higher. The enhanced delignification of prehydrolyzed chips has been attributed to improved permeability of the cell wall caused by increased pore volume, resulting in improved penetration of the cooking liquor, and hydrolytic cleavage of lignin structures and covalent bonds of lignin-carbohydrate complexes (LCC) during pre-extraction (Sixta 2006a). The shortened cooking time could potentially enable a capacity increase in cooking. Reducing the sulfidity level from 40% to 20% in cooking of prehydrolyzed chips (pulps 2 and 3) increases the required H-factor. As expected, the higher sulfidity level would therefore seem to increase the delignification rate in the cooking of prehydrolyzed chips.

As can be seen in Table 2, the yields on wood after cooking of pulps 1 and 2 are 49.5% and 42.3%, respectively. To obtain a similar brownstock pulp production, this 7.2 % percentage unit drop in yield on wood would signify an increase in wood consumption by approximately 17%. This is in agreement with our previous results (Kautto et al. 2010), where a 16% wood consumption increase was calculated based on smaller-scale prehydrolysis and cooking experiments. This would imply that potentially more valuable products than biofuels would need to be produced from at least part of the prehydrolyzate to compensate for the rather significant increase in wood consumption. The determination of the minimal values of the products produced from the prehydrolyzate requires careful economic analysis of the prehydrolysis process. A comprehensive economic analysis of the process is, however, beyond the scope of this study.

The composition of the hydrolyzate was not analyzed in this set of experiments. A thorough mass balance calculation of the prehydrolysis and cooking could not therefore be carried out. However, assuming that 14.1% of wood material (approximately 50% of which being carbohydrates) would be dissolved at P-factor 200 at a temperature of 150 °C as in our previous experiments (Kautto et al. 2010, note a smaller-scale digester, different temperature profile of prehydrolysis and a

different set of raw material), the cooking yield of pulp 2 would be 49.2%. Taking into consideration that the kappa number after cooking was slightly lower with pulp 2, it would seem that the cooking yields of water prehydrolyzed and unhydrolyzed softwood pulps are rather similar. In the literature, prehydrolysis has however been reported to decrease the cooking yield. With 5.0% and 7.0% of loblolly pine pre-extracted in water prehydrolysis at 170 °C, Yoon and van Heiningen (2008) present the yields on wood after cooking to be approximately 42.5% and 39.5%. Based on these extraction amounts and pulp yields, and a yield of approximately 45.5 % of unhydrolyzed pulps at equal kappa numbers, the cooking yields can be calculated to be approximately 0.8 and 2.6 percentage units lower with prehydrolyzed chips. Similarly, cooking yield decreases of approximately 3 to 4% units can be calculated based on the results of Al-Dajani et al. (2009) where 19% of aspen wood was dissolved in water prehydrolysis at 150 °C for 4.5 h prior to cooking. It would therefore seem that pre-extraction of hemicelluloses prior to pulping either leads to degradation of carbohydrates that would be stable in conventional kraft pulping with no pre-extraction in the prehydrolysis stage, or it enhances such degradation in the cooking stage, thus lowering the cooking yield. Based on earlier experiments with a different reactor and a different batch of raw material, a slightly too high assumption of 14.1% of wood extracted in prehydrolysis could possibly explain the seemingly similar cooking yields of unhydrolyzed and prehydrolyzed chips found in this study.

Under constant conditions of oxygen delignification, kappa reduction was significantly higher with prehydrolyzed chips than with reference chips. The kappa number was reduced by approximately 37%, 44%, and 50% with pulps 1, 2, and 3, respectively. This improved response to O₂-delignification allows stopping of the cooking at higher kappa numbers with prehydrolyzed chips. The better response of prehydrolyzed chips to oxygen delignification has previously been shown for *E. saligna* hardwood chips (Sixta 2006b). The increased kappa reduction of hemicellulose-poor prehydrolyzed chips is also in line with the findings of Zou et al. (2002). By varying the xylan content of brownstock hardwood kraft pulp with the use of anthraquinone, they found that a higher amount of xylan decreases the rate of oxygen delignification. This would imply that the amount of xylan affects the accessibility of the chemical reactants in the O₂-stage. The higher kappa reduction of prehydrolyzed pulp 3 than that of prehydrolyzed pulp 2 could probably be explained by the higher kappa number before O₂-stage. It has been shown that a higher kappa number after softwood kraft cooking leads to a higher kappa number reduction in subsequent O₂-delignification (Poukka et al. 1999). Possibly, this is because pulps with higher kappa numbers after cooking contain a larger amount of easily removable lignin fragments. With low residual kappa numbers, pulps have been shown to contain relatively more LCCs that are difficult to delignify (Lawoko et al. 2004).

In addition to kappa number reduction, the response of pulps to O₂-delignification can also be characterized by selectivity. Selectivity is normally defined as the reduction of viscosity per kappa unit. Based on data presented in Table 2, the selectivities of pulps 1, 2, and 3 would be approximately 24.2, 23.1, and 16.2 (Δml/g)/Δkappa, respectively. The selectivity of prehydrolyzed S-40% pulp would therefore seem to be slightly better, and the selectivity of prehydrolyzed S-20% pulp significantly better than that of the reference pulp. Interestingly, selectivity has been reported in the literature to be enhanced with increasing hemicellulose content (Zou et al. 2002; Zou 2002). One explanation for this finding has been that hemicelluloses act to protect the cellulose from radical attack of free hydroxyl radicals (OH·) (van

Heiningen and Violette 2001; Zou et al. 2002), thus hindering cellulose degradation. The peeling reactions of hemicelluloses would also consume alkali, thus decreasing the amount of alkali available to react with cellulose. The amount of cellulose and its degree of polymerization are the major contributors to the viscosity of pulp due to its high degree of polymerization (Zou et al. 2002). Unlike in the experiments of Zou et al. (2002), where initial kappa numbers were low (16.3 to 17.6) and the kappa number reductions in the O₂-stage were rather low and uniform (approximately 35% to 38%), the kappa numbers in this work and consequently also the kappa number reductions were higher. The kappa number reductions also varied more significantly, being higher with prehydrolyzed chips. Although the viscosity loss of pulp 1 (225 ml/g) was lower in the O₂-stage than that of pulps 2 and 3 (250 and 270 ml/g), the selectivities of prehydrolyzed chips were higher. In this work, it would therefore seem that the higher kappa number reductions of prehydrolyzed chips contributed more to the selectivity than the loss of viscosity.

The Effect of Prehydrolysis on Bleachability of Pulps

The term bleachability is used to describe the ease of bleaching of a given pulp, but there is no standard method to evaluate the bleachability of pulps. Usually, bleachability of pulp is the consumption of bleaching chemicals required to reach a given brightness. Results from bleaching of pulps 1, 2, and 3 are presented in Table 3. The chemical consumptions as total active chlorine (kg Cl/ton of pulp) in the DED-bleaching sequence are shown in Fig. 2.

Table 3. Bleaching Chemical Dosages in the DED-sequence and the Development of ISO-brightness and Pulp Viscosity in Bleaching

Pulp	Kappa after O ₂ -stage	Stage	Act. Cl, kg/tp	NaOH, kg/tp	End pH	Brightness, ISO %	Viscosity, ml/g
1	16.1	O ₂		20		37.7	1055
		D ₀	32.2		1.9		
		E		19.3	12.6	54.7	1037
		D ₁	10		3.6	74.1	998
2	13.6	O ₂		20		42.5	1070
		D ₀	27.2		1.7		
		E		16.3	12.5	58.1	1018
		D ₁	10		3.8	73.7	990
3	16.4	O ₂		20		39.4	1010
		D ₀	32.8		1.7		
		E		19.7	12.6	56.2	953
		D ₁	10		3.7	71.9	935

As can be seen in Table 3, pulp 2 had higher brightness and a lower kappa number than pulp 1 after the oxygen delignification stage. Yet, prehydrolyzed pulp 2 did not reach a higher final brightness than unhydrolyzed pulp 1 after DED-bleaching, final brightnesses being 73.7% and 74.1%, respectively. However, the lower kappa number after O₂-delignification of prehydrolyzed pulp 2 enabled a lower ClO₂-charge in the D₀-stage (15.5% lower, calculated as total active chlorine). This resulted in lower total chemical consumption in the DED-bleaching sequence, with no losses in viscosity, when the target was to reach a final ISO-brightness of 74%. At the same

time, pulps 1 and 2 showed no remarkable difference in bleachability calculated as $(OXE/ton)/\Delta\kappa$ in the DED-sequence. Cooking of prehydrolyzed chips with a lower sulfidity level of 20% resulted in a lower final brightness (71.9%) even with the highest chemical charge calculated as total active chlorine.

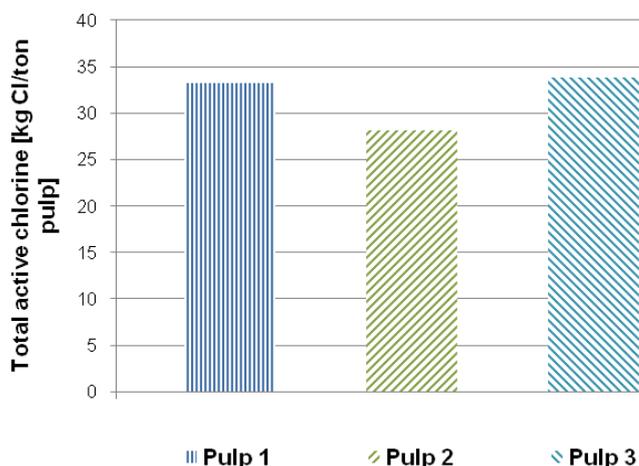


Fig. 2. Total chemical consumption in the DED-sequence calculated as total active chlorine (kg Cl/ton of pulp). Final brightnesses for pulps 1, 2, and 3 were 74.1%, 73.7%, and 71.9%, respectively.

A higher level of hydrosulfide ions in cooking, i.e. higher sulfidity, is known to have a slightly positive effect on unbleached brightness (Axelsson 2004, Gustavsson et al. 1999) and leads to better brightness development during ECF bleaching (Neto et al. 2002; Axelsson 2004). Based on our data, it can be said that the correlation between sulfidity level in cooking and pulp bleachability is markedly the same, whether or not the chips are prehydrolyzed prior to cooking. Figure 3 depicts the brightness gain throughout (O)DED-bleaching and chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp) of unhydrolyzed pulp 1 and prehydrolyzed pulps 2 and 3.

As can be seen in Fig. 3, prehydrolyzed pulp 2 reached the same final brightness in (O)DED-bleaching as unhydrolyzed pulp 1 with lower chemical dosage calculated as total active chlorine (kg C/ton of pulp). Lowering the sulfidity level for prehydrolyzed pulp in cooking from 40% to 20% caused increases in chemical consumption and hindered the attainment of equally high final brightness. The same trend of increased chemical consumption and difficulties in reaching equally high brightness levels as with pulps 1 and 2 was even more pronounced with non-sulfur cooking of prehydrolyzed chips (data not shown).

Since prehydrolysis affects various aspects in the cooking process and pulp composition, some potential indirect effects of prehydrolysis on pulp bleaching will be discussed in the following paragraphs. To analyze the significance of these factors individually requires, however, further studies.

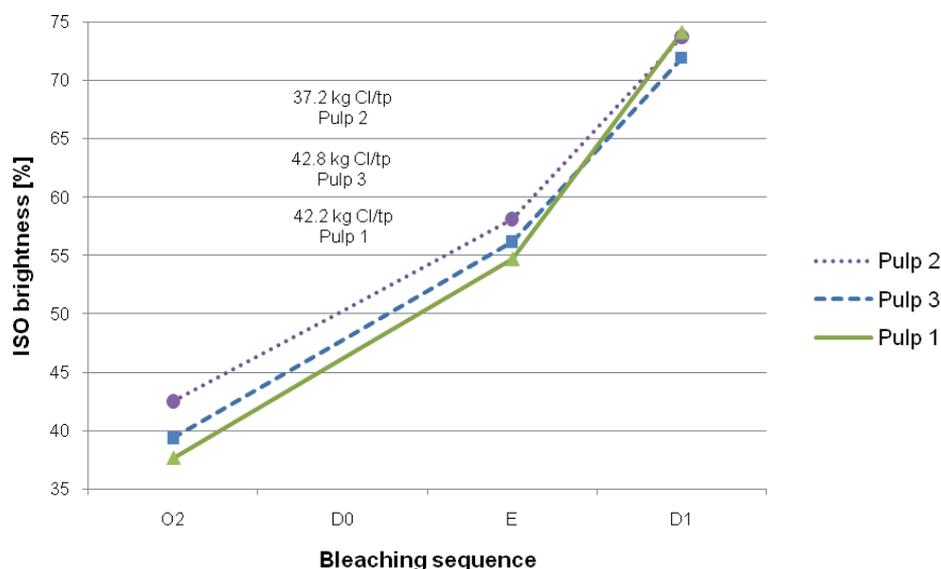


Fig. 3. ISO-brightness development in (O)DED-bleaching for prehydrolyzed pulps with chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp).

Effect of cooking H-Factor on bleachability

Low H-factor is known to be beneficial for the bleaching response of pulp, at least for *Eucalyptus globulus* kraft pulps (Neto et al. 2002). A lower H-factor in cooking also results in a higher amount of alkyl-aryl ether linkages (β -O-4 structures) in residual lignin, and these kinds of pulps exhibit low specific absorption coefficients, i.e. better bleachability (Gustavsson et al. 1999). In the experiments described in this paper the prehydrolyzed pulp 2 was cooked with a lower H-factor than the unhydrolyzed pulp 1; H-factors being 1000 for prehydrolyzed and 1600 for unhydrolyzed pulp. The considerably lower H-factor of prehydrolyzed pulp 2 did not, however, lead to an increase in bleaching response compared with the reference pulp 1. One possible explanation is that the lignin fraction in water prehydrolyzed pulp has already experienced undesirable acid condensation reactions and loss of β -O-4-linkages in the prehydrolysis step, overruling the effect of a lower H-factor in cooking. Structural and chemical changes of lignin and breakage of ether linkages in water prehydrolysis have been suggested also by other authors (Antal 1996; Mosier et al. 2005; Leschinsky et al. 2007; 2008), but the lack of effective analytical methods for evaluating lignin, both its structure and its chemical composition, hinders more complete understanding of this phenomenon (Mosier et al. 2005).

Effect of hexenuronic acids on bleachability

During kraft pulping, 4-O-methylglucuronic acid groups attached to xylan are partially converted to hexenuronic acid groups, forming hexenuronoxylan (Jiang et al. 2000). Hexenuronic acids (HexA) contribute to the measured kappa number in kraft pulps, 3-6 kappa number units for hardwood kraft pulp and 1-3 kappa number units for softwood kraft pulps (Gellerstedt and Li 1996). Based on previous studies (Antonsson et al. 2003; Liu et al. 2009), it is likely that the generation of hexenuronic acids during cooking is lower with prehydrolyzed pulp, since a proportion of

softwood xylan is removed from the wood chips in the prehydrolysis step. Consequently, the amount of 4-O-methylglucuronic acid (MeGlcA) sidegroups attached to xylan are diminished in the pulp by respective ratio, thus lowering the amount of MeGlcA sidegroups converted to HexA during cooking of prehydrolyzed chips.

Hexenuronic acids are known to play an important role in consuming electrophilic bleaching agents such as ozone and chlorine dioxide (Vuorinen et al. 1996) and have been found to be as reactive as lignin towards these electrophilic bleaching chemicals (Vuorinen et al. 1997). In addition to increased consumption of bleaching chemicals, hexenuronic acid groups cause greater brightness reversion and poorer metal removal (Jiang et al. 2000). Therefore, when comparing water prehydrolyzed and unhydrolyzed softwood pulp, the difference in the HexA amount of unbleached pulp might also have an effect on chemical consumption in bleaching. The hexenuronic acid content of the unbleached pulps was not determined in this work, and the significance of this assumption to bleaching results should thus be verified with further studies.

Effect of metal content of pulp

Dahl et al. (1998) have studied the role of transition metal content in the D stages of pulp bleaching. According to these authors, manganese and especially iron in the process water cause loss of brightness; iron also has a detrimental effect on pulp viscosity. Lachenal et al. (1998) reported that iron in chlorine dioxide bleaching may generate $\text{Cl}\cdot$ radicals and therefore cause depolymerisation of carbohydrates, reducing the viscosity of pulp.

According to Sjöström (1993), transition metals in wood and pulp suspensions are partially bound to the carboxyl groups present in xylan and pectins held by the forces complexing the wood constituents, or existing as free ions in the water. Transition metals can easily be displaced and washed out of a pulp suspension (Dahl 1999). Heavy metals such as Fe and Mn can be assumed to be partially washed away somewhat similarly from wood chips in the acidic conditions of water prehydrolysis, since such metal ions can be displaced and washed out from wood by aqueous acids (Sjöström 1993).

In our study the content of the transition metals manganese and copper was lower for prehydrolyzed than for unhydrolyzed pulp, but the amount of iron in prehydrolyzed pulps was markedly higher than for unhydrolyzed pulp (see Table 4 below). High amounts of iron may have hindered the bleachability of the prehydrolyzed pulps. Since the content of other transition metals (Mn, Cu) in prehydrolyzed pulps decreased, it can be concluded that the excess iron was probably derived from the interior wall of the prehydrolysis/cooking vessel under the acidic conditions of the water prehydrolysis. This fact needs to be taken into consideration when designing equipment used for hot-water extraction of wood chips.

Table 4. Metal Contents of Examined Pulps Before Oxygen Delignification

Sample	Fe, ppm	Mn, ppm	Cu, ppm
Pulp 1	11.0	12.1	22.3
Pulp 2	30.7	8.7	9.5
Pulp 3	75.7	7.1	17.2

The Effect of Prehydrolysis on Pulp Properties

Handsheet properties were evaluated for the bleached pulps at an ISO-brightness of 74% for pulps 1 and 2, and 72% for pulp 3. Figure 4 depicts the number of revolutions in a PFI-mill required to achieve a tensile index value of 70 Nm/g for the examined pulps. Tear index values at the corresponding tensile index for each pulp are presented above the columns.



Fig. 4. Required number of revolutions in a PFI-mill in order to achieve a tensile index of 70 Nm/g. Tear index values at the corresponding tensile index are presented above each column. Respective densities for pulps 1, 2, and 3 after beating to a tensile index of 70 Nm/g were 705, 720, and 720 kg/m³, respectively.

As Fig. 4 indicates, prehydrolyzed pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than unhydrolyzed pulp 1 to achieve a given tensile index value. This is in line with previous findings, since shorter beating times and less energy absorption in beating is a feature of kraft pulps having high hemicellulose content (Rydholm 1967; Vaaler et al. 2002; Young 1994). Hemicelluloses contribute significantly to the swelling tendency of fibers. With increased swelling, interfiber contact during beating increases promoting faster external fibrillation and hence better beating response. As reported by Yoon and van Heiningen (2008) regarding slower beating responses for hot-water pre-extracted kraft pulps, the relation between hemicellulose content and beating response has also been observed with low hemicellulose content pulps. The significant reduction in beating response and strength development might present problems in commercialization of prehydrolyzed pulps.

The prehydrolyzed pulps in this study exhibited higher tear index values with the same tensile index value as unhydrolyzed pulp, as can be seen in Fig. 4. Consequently, prehydrolyzed pulps had better strength potential (tensile index x tear index) than unhydrolyzed pulp. Strength potential values were plotted as a function of sheet density (not shown), and the highest strength potential (tensile index x tear index) for both unhydrolyzed and prehydrolyzed pulps was achieved approximately at density 700 kg/m³. Table 5 presents values of pulp properties interpolated to the density value 700 kg/m³.

Table 5. Properties of pulps 1, 2, and 3 at Density 700 kg/m³. Values are Interpolated to the Given Density

Property	Density [kg/m ³]	Pulp 1	Pulp 2	Pulp 3
Cellulose/hemicellulose ratio		4.9	10.6	10.1
Beating revolutions [-]	700	525	2395	1585
CSF [ml]	700	684	668	677
Tensile index [Nm/g]	700	67.1	58.2	62.1
Tear index [Nm ² /kg]	700	16.2	22.6	23.9
Tensile stiffness index [kNm/g]	700	6.87	6.17	6.60
Gurley air permeance [μm/Pas]	700	37.6	42.5	42.1
Light-scattering coefficient [m ² /kg]	700	22.7	23.8	24.2
Opacity [-]	700	69.2	72.0	74.8

Table 5 shows that as approximately half of the hemicelluloses were removed by water prehydrolysis, pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than pulp 1 in order to reach the density level at which the highest value for strength potential was attained. Additional beating of pulps 2 and 3 led to lower pulp freeness (CSF), yet the tensile index of these pulps was lower than for pulp 1.

A decrease in tensile index and an increase in tear index are considered to be the main features of low hemicelluloses content pulps (Kettunen et al. 1982; Molin and Teder 2002; Rydholm 1967; Spiegelberg 1966). As can be seen in Table 5, these features were also observed in this study. Tensile stiffness index was also affected. Partial removal of hemicelluloses by prehydrolysis lowers the tensile stiffness index value. The tensile stiffness index is defined as the maximum angular coefficient in the stress-strain curve of the paper. The major factor affecting this angular coefficient is the amount of fiber-to-fiber bonding (Giertz and Rodland 1979); the stronger the fiber-to-fiber bonding, the higher the maximum angular coefficient. This leads to an assumption that fiber-to-fiber bonding in the fiber network is diminished in sheets made from prehydrolyzed pulp. Reduced fiber-to-fiber bonding has been reported to decrease tensile index values (Rydholm 1967) and increase tear index values (Bronkhorst and Bennett 2002). The decreased tensile index and increased tear index of this study would therefore also support the assumption that prehydrolysis reduces fiber-to-fiber bonding in the fiber network. Also Yoon and van Heiningen (2008) have suggested that the negative effects of hot-water pre-extraction on tensile strength of kraft pulps could be explained by the low interfiber bonding ability of the hemicellulose-poor pulps.

Prehydrolyzed pulps 2 and 3 formed sheets with a higher light-scattering coefficient (LSC), opacity and air permeability than unhydrolyzed pulp 1. The optical properties, LSC and opacity, were even better when prehydrolyzed pulp was cooked at a lower sulfidity level, 20% instead of 40%. Compact, narrow, and thick-walled fibers are known to form a porous paper that has high ability to scatter light.

Therefore, the dimensions of prehydrolyzed softwood fibers had likely changed compared to unhydrolyzed fibers, enabling more opaque, porous, and light-scattering sheets. Similar properties for paper sheets with various hemicellulose contents have also been reported by Hunger (1983) and Santos et al. (2008). Increased LSC and opacity also indicate decreased interfiber bonding in sheets made from prehydrolyzed pulps, since increasing interfiber bonding with fibrillar fines is known to have a negative effect on LSC (Luukko and Paulapuro 1999), and opacity is increased by decreasing interfiber bonding with debonding agents (Talaiepoor and Imani 2008). Therefore, differences in interfiber bonding are likely to be the main cause for the differences in the paper properties between prehydrolyzed and unhydrolyzed pulps.

CONCLUSIONS

1. The cooking of prehydrolyzed chips is significantly faster than that of unhydrolyzed chips. To obtain similar kappa numbers at similar cooking temperatures, the prehydrolyzed chips require approximately 40% shorter cooking times.
2. Prehydrolysis at P-200 decreases the pulp yield on wood by approximately 7.2 percentage units.
3. The response to oxygen delignification is higher with prehydrolyzed chips, allowing cooking to be stopped at higher kappa numbers.
4. The same final brightness (74% ISO) in (O)DED-bleaching can be reached with lower chemical consumption when wood chips are prehydrolyzed prior to cooking and cooked with a similar sulfidity level.
5. Prehydrolyzed pulps require considerably more beating to reach a specific pulp freeness (CSF) or tensile index than unhydrolyzed pulp, but exhibit higher strength potential (tensile index x tear index) at given densities.

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Characteristics of prehydrolysis-kraft pulp fibers from Scots pine

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Abstract

To clarify the influence of prehydrolysis on fiber characteristics, Scots pine (*Pinus sylvestris* L.) wood chips were subjected to pressurized hot-water and dilute-acid prehydrolysis (0.5% H₂SO₄) prior to kraft pulping to partially remove hemicelluloses as hydrolyzate. After the prehydrolysis, the wood chips were submitted to kraft pulping and the pulp was fully bleached in oxygen (O), chlorine dioxide (D), alkaline extraction (E) and chlorine dioxide (D)-sequence. Measurements with an automated optical fiber analyzer showed that prehydrolysis prior to kraft pulping caused significant changes in the fiber dimensions and morphology of the final bleached pulp. Especially, a decrease in fiber width and an increase in fiber deformations were observed compared to a reference kraft pulp. The scanning electron microscopy of handsheets supported the morphology analyses and revealed alterations also in the fiber ultrastructure. The changes in both chemical and physical fiber characteristics require attention when considering the correct processing and end-use of prehydrolysis-kraft pulp fibers.

Keywords: biorefinery; deformation; fiber damage; hemicelluloses; papermaking properties; pine; prehydrolysis; prehydrolysis-kraft pulping.

Introduction

A growing interest in the utilization of lignocellulosic biomass has led to the development of various biorefinery concepts (Kamm and Kamm 2004; Kamm et al. 2006; Dautzenberg et al. 2011; Hörhammer et al. 2011; Schrems et al. 2011; Telysheva et al. 2011). In kraft pulp (KP) production, substantial amounts of hemicelluloses are dissolved in the pulping

liquor. These and other dissolved materials (mainly lignin) are incinerated in the recovery furnace. The heating value of hemicelluloses (13.6 MJ kg⁻¹) is only about half of that of lignin (27 MJ kg⁻¹). As an alternative, hemicelluloses could be recovered as oligomeric and monomeric sugars prior to pulping (van Heiningen 2006). The pre-extracted products could be converted to ethanol through fermentation or used as a feedstock for production of more value added chemicals (Wärpy et al. 2004).

Removal of hemicelluloses prior to pulping is known as prehydrolysis (PreH), which is based on the pioneering work of Richter (1931, 1932a,b). Since then, numerous PreH processes are documented in studies and reviews. Pretreatment with diluted acids, hot-water (autohydrolysis), or steam are described (e.g., Richter 1956; Rydholm 1967a; Casebier et al. 1969; Carrasco and Roy 1992; San Martín et al. 1995). Also more recent papers document the importance of this topic (Frederick et al. 2008; Leschinsky et al. 2009; Leppänen et al. 2011; Song et al. 2011; Testova et al. 2011; Yoon et al. 2011). Generally, a PreH process is aiming at the production of dissolving-grade pulps with low-hemicellulose content. Recently, the PreH technology has gained renewed interest also as a means to separate hemicelluloses for biofuels or biochemicals production in combination with paper-grade pulp production by kraft process. So, the production of special-grade pulps, in which some of the hemicelluloses are not desired, would be possible.

PreH influences many aspects of the fiber line and paper-making properties of the KP (Richter 1956; Annergren et al. 1965; Jacopian and Casperson 1966; Yoon and van Heiningen 2008; Kautto et al. 2010b). Al-Dajani and Tschirner (2010) called attention to the fact that PreH may also damage and deform the cellulosic fibers, which affect the physical properties of the fiber network in a paper sheet (Page and Seth 1980; Page et al. 1985a; Nyholm et al. 2001). In industrial pulping processes, the treatment of fibers in mixers, pumps, and blow line valves cause additional mechanical damages of the fibers (MacLeod et al. 1987; MacLeod 1995). The strength of softwood (SW) fibers from the fiber line is only 60–75% of the overall strength potential of the fibers (MacLeod 1995; Tikka and Sundquist 2001). Fiber deformation is an important factor in this regard (Rauvanto 2010).

The hemicellulose content influences the deformation tendency of the fibers (Page et al. 1985b). According to Brännvall and Lindström (2007), SW fibers with a high xylan content are able to endure mechanical treatment better than fibers with a lower xylan content as the latter suffer more local fiber wall defects. Rauvanto et al. (2006) reported similar findings for enzymatically treated SW fibers: fibers with a low hemicellulose content were more susceptible to mechanically-induced

deformation during oxygen delignification. To know more about the chemical and physical characteristics of PreH-KP fibers could be important concerning their suitability for different applications.

The objective of this work was to clarify the effect of hot-water and dilute-acid PreH prior to the kraft pulping of pine wood chips on fiber characteristics both from the chemical and physical point of view. This paper focuses on the characteristics of PreH-KP, fiber morphology, and three-dimensional fiber damage in particular.

Materials and methods

Materials

The wood (*Pinus sylvestris* L.) was purchased as logs from Kartiopuu Oy, Lappeenranta, Finland. The logs were debarked with a rotor debarker and chipped with a Bruks 1702M disk chipper (Bruks AB, Sweden). The chip lot was further screened in a chip classifier specified in SCAN-CM 40:01. The accept fractions (13 mm Ø and 7 mm Ø) were mixed. Acetone-soluble matter, total lignin and carbohydrate content were determined according to SCAN-CM 49:03, TAPPI-T 222 om-02 and SCAN-CM 71:09, respectively (Table 1).

Wood chip pretreatments

The pretreatment and cooking conditions applied in this study were determined based on the studies of Kautto et al. (2010a,b). In the PreH, 4500 g of pine wood chips were placed in a 30-l digester. Deionized water (at 80°C) was then introduced into the digester to obtain a liquor-to-wood ratio of 4.6 l kg⁻¹. In the dilute-acid PreH, 0.5% H₂SO₄ o.d.w. was added together with deionized water. The mixture was heated to 150°C at a rate of 2°C min⁻¹. The mixture was kept at 150°C for 93 min in the hot-water PreH and 35 min in the dilute-acid PreH.

Brasch and Free (1965) introduced the PreH factor as a measure of the severity of a PreH treatment. Lin (1979) subsequently determined the activation energy for the cleavage of glycosidic bonds of the carbohydrate material in the wood, and coined the term P-factor for the hydrolysis process. The P-factor is given by the following expression (Sixta 2006):

$$P\text{-factor} = \int_0^t \frac{k(T)}{k_{100^\circ\text{C}}} dt = \int_0^t e^{40.48 - \frac{15106}{T}} dt \quad (1)$$

where t is the reaction time in hours, T is the temperature in Kelvin, and k is the rate constant. The P-factors were calculated from the

Table 1 The relative chemical composition of the raw material, Scots pine (*Pinus sylvestris* L.) chips.

Material	(%)
Acetone-soluble	2.4
Total lignin	26.1
Cellulose ^a	42.8
Xylan ^a	8.1
Glucmannan ^a	16.9
Other polysaccharides ^a	2.7
Sum	99.4

^aThe polysaccharide composition was calculated according to Janson (1974).

recorded temperature/time data according to Eq. 1 based on an activation energy of 125.6 kJ mol⁻¹ (or 30 kcal mol⁻¹). In this study, the hot-water and dilute-acid PreH processes correspond to P-factors of 200 and 80, respectively.

After PreH, the hydrolysis liquor (undiluted prehydrolyzate) was drained from the digester. To determine the yield of the wood residue, the rest of the hydrolyzate entrapped in chip pores was separated by a washing procedure: the digester was filled with 11 l of deionized water at 100°C, and after 10 min, the wash filtrate was drained from the digester. The washing procedure was repeated three times. The yield of the wood residue is reported as the oven-dry (o.d.) weight of the wood residue in relation to the o.d. weight of the initial wood. Thereafter, the prehydrolyzed wood chips were discarded.

For cooking, the hot-water and the dilute-acid PreH were carried out again. After draining the hydrolysis liquor (undiluted prehydrolyzate), the prehydrolyzed wood chips were subsequently cooked and bleached without intermediate washing. The washing stage was excluded in order to achieve a minimal amount of unwanted lignin condensation reactions that could hinder the delignification of prehydrolyzed wood chips. Therefore, only undiluted hydrolyzate was collected prior to the cooking. The undiluted prehydrolyzate and the wash filtrates were stored in a freezer and not analyzed in detail within this study.

Cooking

Untreated reference chips and pretreated chips were cooked in the same digester as was used for the PreH. For the reference cook, after introducing deionized water and the cooking chemicals, the digester was heated from 20°C to 160°C at a rate of 1.5°C min⁻¹. For the prehydrolyzed chips, deionized water and cooking chemicals were pumped into the digester at the cooking temperature 160°C and no additional heating period of the digester was therefore needed. The pulp kappa number, brightness and viscosity were measured using standard ISO methods (302:2004, 2470:1999 and 5351-1:2010, respectively). The total yield was defined as the ratio of the mass sum of o.d. screened pulp plus rejects to the mass of o.d. initial wood. For details see Table 2.

Bleaching

All pulps were oxygen delignified to the target kappa number of 15±1 and subsequently bleached to full brightness in a DED-sequence. The chemical charges in the bleaching stages D₀ and E were calculated from the kappa number after O₂-delignification. The chemical charge in the D₁-stage was determined as to attain the target ISO-brightness (88%). For details see Table 3.

Table 2 Cooking conditions.

Parameters	Prehydrolysis (PreH) with		
	No PreH	Hot-water	Dilute-acid
H-Factor	1600	1250	1250
Sulfidity	35	35	35
Temp. (°C)	160	160	160
L/W ratio	4.6	4.6	4.6
EA ^a (%)	20	20.8	22
Kappa target	25±2	25±2	25±2
Res. alkali targ.	8	8	8

^aEffective alkali.

Table 3 Oxygen delignification and bleaching conditions with chemical charge amounts.

	Bleaching steps			
	O ^a	D ₀	E	D ₁
Pulp consistency (%)	12	9	10	9
Act. Cl charge (%)		0.24× kappa		Ref: 2.75 PHW: 2.45 DA: 2.01
NaOH charge (%)	Ref: 1.45 PHW: 1.35 DA: 1.21		0.35× D ₀ charge	
Temp. (°C)	90	60	70	70
Time (min)	60	60	60	180
Pressure (bar)	8			
Final pH		2.1–2.2	10.5–10.9	3–3.5

^a0.5% Epsom salt was added in the O₂-stage to protect the fibers. Ref, unhydrolyzed; PHW, pressurized hot-water; DA, dilute-acid.

Pulp analyses

Fiber properties such as the kink index, curl, fiber length and width were determined with the Kajaani FS-300 (Metso Automation, Finland), which is an automated optical fiber analyzer. The fiber morphology and the overall condition of the fibers were also evaluated by scanning electron microscopy (SEM): JEOL 5800 SEM (JEOL Ltd., Tokyo, Japan) with a 10-kV accelerating voltage and a 10-mm working distance.

The chemical compositions of the bleached pulps and water retention values (WRV) from the fiber suspensions were determined and the handsheets for the physical testing of non-beaten pulps were made according to SCAN-CM 71:09, SCAN-C 62, EN ISO 5269-1:1998, respectively.

Results and discussion

Prehydrolysis-kraft pulping and (O)DED-bleaching of the pulps

The results from cooking, oxygen delignification, and bleaching presented in Table 4 are in agreement with those reported in several previous studies on the PreH of wood chips and subsequent alkaline cooking. Acetic and other organic acids liberated through the cleavage of O-acetyl and uronic acid substitutions lowered the pH of the hot-water PreH process and the prehydrolyzate to 3.7. These acidic PreH conditions partially dissolve hemicelluloses and also render the remaining hemicelluloses to be more easily dissolved in the subsequent alkaline cook (Bernardin 1958; Brasch and Free 1965). Consequently, hot-water PreH decreased the overall brown-stock pulp yield on wood, as was observed by Yoon and van Heiningen (2008). Adding a catalyst (H₂SO₄) increased the rate of dissolution of material during the PreH, but also lowered the pH of the hydrolysis process and the hydrolyzate to below 3. More severe conditions in the PreH caused by the addition of a catalyst cause some cellulose degradation (Carrasco and Roy 1992) and pronounced alkaline degradation in the subsequent cook (Jacopian and Caspersen 1966; Rydholm 1967a). The degradation of cellulose is further

indicated by the decreased viscosity of the dilute-acid PreH-pulp, whereas the stability of cellulose in the hot-water PreH was higher. However, values for the degree of polymerization (DP) of cellulose calculated according to Da Silva Perez and van Heiningen (2002) indicate that also hot-water PreH decreased the DP of cellulose compared to the reference cook. The PreH of wood chips reduced the cooking time (H-factor) required for reaching the target kappa number, as reported earlier for softwood (Chirat et al. 2009; Kautto et al. 2010a), eucalyptus (Sixta 1996) and sugar maple pulp (Amidon et al. 2006). Prehydrolyzed pulps were also easier to bleach than the reference pulp, which is in agreement with the findings of others (Amidon et al. 2006; Colodette et al. 2011).

Fiber characteristics of non-beaten pulp samples

The non-beaten PreH-pulp fibers were more curled and much more kinked than fibers in the reference KP (Table 4). The kink indices for non-beaten bleached fibers were 824, 1439, and 1661 l m⁻¹ for the unhydrolyzed reference, the hot-water PreH-, and the dilute-acid PreH-pulp, respectively. However, the curl indices are not too different: compared to the reference KP the hot-water PreH- and dilute-acid PreH-pulp show 32% and 37% higher values, respectively. Apparently, alkaline cooking preceded by PreH causes more clearly measurable angles (kinks) in the 3D fiber shape rather than just gently curling the fibers.

The length and width of bleached pulp fibers were reduced by PreH prior to pulping. Kinks and other abrupt changes in the 3D fiber shape are known to lead to some inaccuracy in the contour length measurement of pulp fibers with automated optical analyzers. Therefore, the fiber length results for hot-water and dilute-acid PreH-pulps shown in Table 4 should be regarded as a hint of fiber deformations rather than as a reliable measure for the reduction in the actual fiber length. The decrease in fiber width of both PreH-pulps shows changes in the cell wall structure. Obviously, the remaining polysaccharides after PreH became more susceptible to degradation in subsequent alkaline cooking, and the removal of interstitial

Table 4 Pulping, (O)DED-bleaching and characteristics of unhydrolyzed, pressurized hot-water and dilute-acid prehydrolyzed pine wood.

Property	Prehydrolysis (PreH) with		
	No PreH	Hot-water	Dilute-acid
Yield of wood residue (%)	100	88.5	83.8
Hydrolyzate pH	–	3.7	2.4
Pulp after digester			
Kappa number	25.4	27.7	27.2
Residual alkali (g NaOH l ⁻¹)	7.96	8.09	9.10
Consump. of EA (% NaOH)	16.3	17.1	17.8
Viscosity (ml g ⁻¹)	1230	1330	1140
ISO-Brightness (%)	31.2	29.9	32.1
Yield on wood (%)	46.9	42.1	39.5
Pulp after O ₂ -stage			
Kappa number	15.3	15.1	13.4
Viscosity (ml g ⁻¹)	1080	1100	1010
ISO-Brightness (%)	33.9	34.1	36.2
Yield on wood (%)	46.3	41.2	38.6
Pulp after DED-bleaching			
Viscosity (ml g ⁻¹)	970	960	900
DP of cellulose ^a	4432	3969	3567
ISO-Brightness (%)	87.6	87.1	87.8
Consumption of ClO ₂ , as tot. active Cl (kg Cl t ⁻¹ pulp)	60.2	59.0	49.3
Cellulose ^b (%)	82.5	90.7	93.8
Glucomannan ^b (%)	8.6	5.1	2.6
Xylan ^b (%)	8.9	4.2	3.6
Tot. amount of hemicellul. (%)	17.5	9.3	6.2
Ratio cell./hemicelluloses	4.71	9.75	15.13
L.w. fiber length (mm)	2.03	1.93	1.88
Fiber width (μm)	25.6	25.0	24.6
L.w. fines content (%)	2.66	2.48	2.20
Kink index (1 m ⁻¹)	824	1439	1661
Fiber curl (%)	17.9	23.6	24.6
WRV (g/g)	1.67	1.56	1.55
Apparent bulk-dens. (kg m ⁻³)	618	570	560
CSF (ml)	710	720	715
Tensile index (Nm g ⁻¹)	34.2	19.0	19.2
Tear index (Nm ² kg ⁻¹)	21.3	14.8	13.3
Tensile stiffness i. (kNm g ⁻¹)	4.71	3.03	3.04
Stretch (%)	3.3	2.3	2.2
TEA index (J g ⁻¹)	0.870	0.340	0.334
IB ^c , Scott-Bond (J m ⁻²)	168	127	112
Air resistance, Gurley (s)	0.8	0.5	0.5

^aCalculated according to Da Silva Perez and van Heiningen (2002). ^bCalculated according to Janson (1974).

^cInternal bond strength. L.w.: length weighted.

material reduces the fiber width. As indicated by the width reduction, in the case of the dilute-acid PreH-pulp the dissolution processes were more intense.

PreH-KPs had a lower content of hemicelluloses than the reference KP (see Table 4). According to Duchesne et al. (2001), the fibrils of never-dried PreH-KP appear to aggregate and form a more compact fiber surface structure compared to the never-dried reference KP. Drying-induced hornification has a similar mechanism in creating interfibril aggregation (Weise 1998). As a consequence of hornification, once-dried KP fibers also have a much more compact surface ultrastructure (Daniel and Duchesne 1998) and a lower WRV than never-dried KP (Cao et al. 1998). As shown in Table 4, the

WRV of the PreH-pulps was lower than that of the reference. Thus, similar differences can be seen in the fiber ultrastructure and WRV between fibers of never-dried PreH-KP and never-dried KP, and between once-dried KP and never-dried KP. It seems to be that never-dried PreH-KP fibers might have somewhat similar fiber-water interaction behavior as once-dried and rewetted KP fibers.

SEM images of freely dried handsheets are presented in Figure 1. Figures 1a,c,e show the morphological differences in the fibers after they have formed a fiber network. The reference handsheet, Figure 1a, differs in appearance from the hot-water and dilute-acid PreH-pulp handsheets, see, Figures 1c,e, respectively. The reference pulp fibers

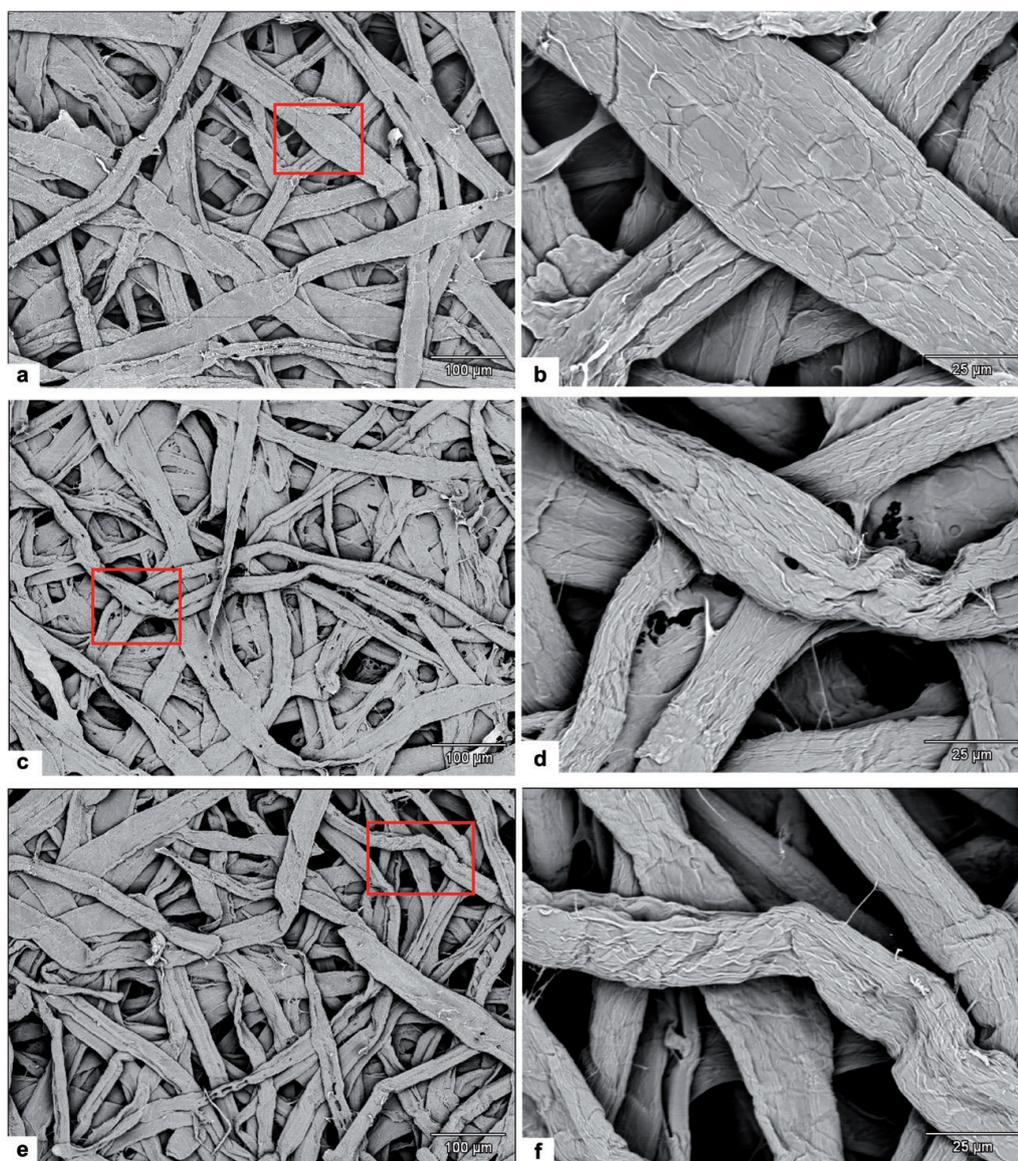


Figure 1 SEM-images from handsheets dried at room temperature with a grammage of 60 g m^{-2} . (a) and (b) reference samples; (c) and (d) hot-water prehydrolyzed kraft pulps; (e) and (f) dilute-acid prehydrolyzed kraft pulps. The red squares indicate the regions magnified on the right-hand side.

seem straighter than those in the PreH-pulp handsheets and they are more evenly aligned in the web and support the morphology analyses. Damaged fibers are more frequent in the PreH-pulps than in the reference. Furthermore, a larger number of compact and narrow fibers can be seen in the PreH-KP handsheets than in handsheets made from the reference. Accordingly, the decrease in fiber dimensions,

especially in the fiber width, is even more pronounced when the PreH-KP fibers are dried.

A closer view of the fiber wall structure shows that kinks, twists, and even micro-ruptures are visible in the 3D structure of the PreH-KPs. As described above, also here the surface structures suffered more in case of PreH-KP samples (Figures 1d,f) than in the reference pulp sample (Figure 1b). High

content of hemicelluloses can inhibit drying-induced fibril aggregation (Hult et al. 2001; Köhnke and Gatenholm 2007). The fiber wall ultrastructure of the dried PreH-KP fibers in Figure 1 seems less uniform than in the reference pulp fibers, indicating pronounced fibril aggregation caused by a low content of hemicelluloses in PreH-KPs.

The results obtained by fiber analyzer and SEM-imaging evidently shows that PreH-KP fibers were more deformed than the reference. Nyholm et al. (2001) have reported that fiber deformations and dislocations can act as reactive sites, thus, making the fibers more sensitive to a chemical attack. Arndt et al. (2011) have suggested that the introduction of mechanical fiber wall damage during pulping could be responsible for achieving lower energy requirements during post-refining and the more homogenous structure of microfibrillated cellulose (MFC). Therefore, the physical characteristics of PreH-KPs could be advantageous in certain conventional or novel applications, when fiber deformations are part of the concept.

Paper properties of non-beaten pulp samples

Compact and slender fibers are known to form a porous and bulky paper, while deformations in fibers increase the paper bulk. The more narrow and deformed PreH-KP fibers should have an influence on the density and air resistance (Table 4).

All of the strength properties of the PreH-pulps are lower than those of the reference (Table 4). Mohlin et al. (1996) found that kinks, angular folds, and twists have a negative effect on properties such as the zero-span tensile strength, tensile index, and tensile stiffness index. High content of hemicelluloses in KP elevates the tensile index and tensile stiffness index of paper (Molin and Teder 2002). Consequently, the greater amount of fiber deformations and the lower content in hemicelluloses in the hot-water and dilute-acid PreH-pulps both contribute to the strength properties loss shown in Table 4.

According to Page et al. (1985a), an increase in stretch is a feature of papers made of kinked and curled fibers, which have to be straightened before they are able to carry a load. In this study, the stretch values were also lower for the PreH-KPs than for the reference. The tensile stiffness index and Z-directional strength (Scott-Bond) values of PreH-KP handsheets indicate that the fiber-to-fiber bonding in the fiber network was diminished. The low content of hemicelluloses is the reason why the kinked and curled fibers did not increase the stretch of the PreH-KP handsheets. Generally, a decrease in the tensile index and an increase in the tear index are considered to be the main features of pulps with a low content of hemicelluloses, e.g., in PreH-KP (Rydholm 1967b; Kettunen et al. 1982; Molin and Teder 2002). It is noteworthy that for the non-beaten PreH-KPs studied in this paper, also the tear index was lower than that of the reference.

The lower strength properties of papers made from non-beaten PreH-KPs are a challenge for the technical and economical feasibility of producing PreH-KP targeted for paper and paperboard production. However, as the initial fiber properties of PreH-pulps are also markedly different from those of the reference, the development of novel refining techniques

that are more suitable for PreH-pulps could offer possibilities for their commercialization in papermaking.

Conclusions

The PreH of wood chips led to a loss in cooking yield and lowered the content of hemicelluloses of the final pulp. PreH-kraft pulping and subsequent bleaching led to changes in the fiber morphology and decreased all strength properties of non-beaten pulp. Apparently, never-dried PreH-KP fibers have fiber-water interaction behavior similar to that of once-dried and rewetted KP fibers. The lower amount of hemicelluloses in the PreH-KPs made these pulps more susceptible to fiber damages than the reference pulp. SEM images of handsheets facilitated the interpretation of the physical measurements. The effects observed on a laboratory-scale are expected to be more severe in industrial production, where pumps, mixers and other equipment can induce further differences in the morphological and physical character of the fibers.

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PUBLICATION III

**Alkaline xylan extraction of bleached kraft pulp -
effect of extraction time on pulp chemical composition and physical properties**

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Alkaline xylan extraction of bleached kraft pulp – effect of extraction time on pulp chemical composition and physical properties

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ABSTRACT: In this pilot scale study, we examined the effects of alkaline extraction time on xylan removal, pulp and paper properties, and the consequences that need to be addressed when scaling up and intensifying the process. Alkaline extraction of bleached birch kraft pulp yields two fractions: pure polymeric xylan and pulp with reduced xylan content. Our results indicate that a similar amount of xylan can be extracted in 5 min as the amount obtained in 60 min. We found, however, that the shorter extraction time is beneficial to maintain the fiber and paper properties at an acceptable level. This pilot trial demonstrated that the washing procedure of the alkali-treated fibers must be selected with care to avoid causing mechanical damage to fibers and to avoid the loss of fines.

Application: Using a shorter alkaline extraction time could simplify process extraction arrangements significantly and make it more attractive economically.

Many pulp and paper industry companies are struggling with declining profits and challenges to their external operations. At the same time, global climate change and awareness of the finite nature of fossil fuels is propelling the development of green technologies and increasing the use of renewable resources in production of both fuels and chemicals. Therefore, companies in the pulp and paper industry must reconsider current strategies. One alternative for increasing the value creation potential might be to seek sustainable competitive advantages from forest biorefining operations [1]. Thus, an integrated forest biorefining (IFBR) concept in which the biorefining technologies would be integrated with existing pulp and paper operations has recently gained interest in academia and the industry to achieve more efficient use of wood-derived biomass [2]. One suggested technology for the next generation IFBR is the integration of the hemicellulose extraction process step into an existing kraft pulp line, allowing the co-production of pulp and hemicellulose-based chemicals.

Hemicelluloses are the second most abundant biomass-based polysaccharide in the world after cellulose. In wood, they comprise about one third of the dry weight. The predominant type of hemicelluloses in hardwoods is *O*-acetyl-(4-*O*-methylglucurono)xylan, or simply xylan. Thus, an existing fiber line producing bleached hardwood kraft pulp represents an attractive source for the industrial-scale production of xylan. Consequently, several options for extracting xylan from the kraft pulp mill material streams have been proposed: from wood chips by a prehydrolysis

process before cooking [3,4], from early cooking liquor [5,6], from weak black liquor [5,7], from LignoBoost filtrate [8], or from bleached hardwood kraft pulp [9,10]. When connecting these xylan extraction processes to the kraft process, the considerable value potential of utilizing the xylan fraction should be realized to maintain an economically feasible process. Therefore, when a xylan product of high purity is targeted, xylan extraction from bleached pulp seems to be the most reasonable option, because no expensive purification steps are needed to remove the lignin and other contaminants present in the prehydrolyzates and cooking liquors.

Alkaline extraction of xylan from bleached birch kraft pulp xylan is reported to yield a high molar weight xylan in a pure polymeric form [9,10], which might be advantageous in terms of the further processing of xylan. Traditionally, the industrial use of xylan has mainly concentrated on its conversion into furfural and xylitol. Xylan and xylan derivatives also have been investigated widely as a functional additive in papermaking purposes in the past [11,12] and recently [13-15]. However, several other possibilities to exploit this valuable raw material have been reported. Besides using xylan for papermaking purposes, potential end uses for xylan-based products include films and barrier coatings [16-18], hydrogels [19,20], foods [21], and even pharmaceuticals [22]. Therefore, alkaline extraction of xylan from bleached birch kraft pulp might provide significantly improved industrial profitability by offering companies new sources of revenue.

In addition to the production of xylan, the integrated alkaline extraction of bleached pulp allows simultaneous produc-

EXTRACTION

tion of birch kraft pulp with reduced xylan content. According to our previous studies, this fraction could be used to replace a part of the unextracted birch pulp in a papermaking furnish [23]. To our knowledge, despite many laboratory studies on the effects of partial xylan extraction on pulp properties [10,24,25] and studies concerning the use of the extracted xylan product [11-22,26], the possibility of implementing the alkaline extraction process of birch kraft pulp on a larger scale has not been published. Although the end application frequently has been addressed, an industrially applicable process solution is still lacking. The aim of this study was to explore and develop the scale-up and process intensification of an alkaline extraction process to a pilot level concept. To produce birch kraft pulp with low xylan content to be used as a raw material in a papermaking furnish, particular attention was paid to the effect of extraction time on xylan dissolution. In addition, important aspects were addressed in relation to the effect of alkaline extraction on pulp and fiber properties.

MATERIALS AND METHODS

An industrial dried ECF bleached birch kraft pulp containing 74.6% cellulose, 24.9% xylan, and 0.5% glucomannan was obtained from a Finnish pulp mill. The alkaline extraction was carried out on a pilot-scale LC-loop for low consistency flows at FiberLaboratory, Mikkeli University of Applied Sciences, in Savonlinna, Finland.

Pulp extraction

Two 7.75 m³ pulper batches, each containing 332.5 kg of o.d. pulp, were first prepared using a vertical pulper (pulp consistency 4.29%). The two batches were then combined and transferred to a 30 m³ storage tank.

The alkaline extraction was carried out in the 30 m³ extraction tank, which was equipped with a Sulzer Salomix SLF chest agitator (Sulzer Pumps; Winterthur, Switzerland). We first diluted 0.75 m³ of a 50% sodium hydroxide solution in the tank with 9 m³ of cold water. When the temperature of the alkali solution was decreased to about 25°C, the pulp was fed into the extraction tank. Filling the extraction tank with

the slushed pulp took 6.30 min. When all the materials were in the extraction tank, the extraction time count was started. The circulation of the pulp from the bottom of the tank to the top of the tank (circulation loop) was initiated with a volume flow of 33.5 L/s, and the rotor speed of the mixer was adjusted to 815 rpm. Other conditions included sodium hydroxide concentration in the extraction of 0.56 M, pH of 12.5, 24.1°C temperature, 2.6% pulp consistency, and 25.5 m³ total volume of the suspension.

After an extraction time of 60 min, the pulp was immediately washed using a pressure-fed MicroScreen (Andritz; Graz, Austria) having 100 micron plate openings. Washing, with a volume flow of 33.5 L/s (washing loop), was continued until the pH of the pulp suspension was below 10. **Figure 1** shows the extraction and washing procedure.

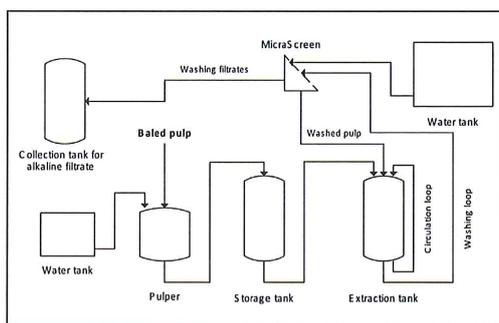
Sampling

Pulp samples were collected after 5, 10, 20, 30, 45, and 60 min extraction from the circulation loop pipeline of the extraction tank (Fig. 1). The pulp samples were washed with tap water immediately after sampling using a Büchner funnel equipped with a Tamfelt Gapmaster Pro F35654GM commercial wire (Metso; Helsinki, Finland). The first filtrate was immediately returned to the funnel and rapidly filtrated through the formed cake to preserve the fines in the pulp samples. A part of the first filtrate was recovered for further investigation. The pulp cakes were washed in the funnel with tap water until the pH of the filtrate was below 8. To determine the extraction yield, the pulp cakes were dried at 105°C and weighed. A similar washing procedure in the Büchner funnel was performed for the MicroScreen-washed pulp to minimize the effect of the sampling procedure on comparability of the results.

Methods

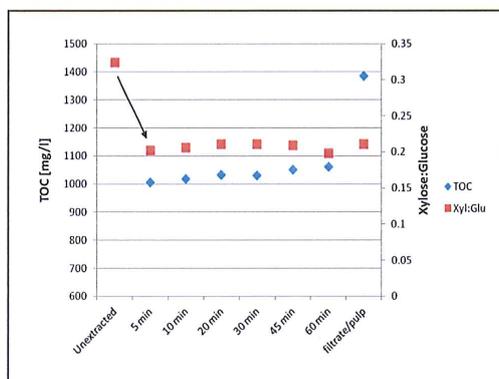
We calculated the xylose-to-glucose ratio (XGR) of the pulp samples based on the relative monosaccharide composition of the pulp samples after acid hydrolysis (SCAN CM 71:09, "Carbohydrate composition"). A high pressure liquid chromatography (HPLC) device equipped with a Varian MetaCarb 87P analytical column (7.8 mm x 300 mm, 20.0 µL) from Agilent Technologies (Santa Clara, CA, USA), and a refractive index detector was used for the detection of monosaccharides from the hydrolyzates. Before injection into the HPLC device, the hydrolyzates were filtered through a 0.2-micron cellulose acetate membrane filter and diluted using ultrapure water. HPLC separation of monosaccharides was carried out at a column temperature of 80°C and flow rate of 0.4 mL/min for 35 min. The injection volume was 10 µL. Ultrapure water was used as an eluent in separation.

Fiber properties were determined using an optical fiber analyzer. Pulp viscosity was determined according to ISO 5351:1, "Determination of limiting viscosity number in cupriethylenediamine (CED) solution." The water retention value (WRV) was determined according to ISO 23714, "Determination of water retention value (WRV)," and the Schopper-



1. The procedure used for the pulp extraction and washing of the alkaline extracted pulp.

EXTRACTION



2. The effect of extraction time (0-60 min) on the xylose-to-glucose ratio (XGR) of pulp samples and the total organic compounds (TOC) content of corresponding alkaline filtrates.

Riegler (SR) number was determined according to SCAN-C 19:65, "Determination of drainability - Part 1: Schopper-Riegler method." Handsheet preparation and testing of paper properties were performed according to EN ISO 5269-1:1998, "Preparation of laboratory sheets for physical testing -- Part 1: Conventional sheet-former method," from pure pulp samples without any addition of chemicals.

The total organic carbon (TOC) in the first filtrates from the Büchner filtrations was determined using a TOC analyzer. Before the TOC analyses, the pH of the filtrates was adjusted to 9 using dilute hydrochloric acid.

RESULTS AND DISCUSSION

Effect of extraction time on xylan dissolution

Figure 2 shows the XGR of the pulp samples and the TOC load in the corresponding alkaline filtrates. During the first 5 min of the extraction, the XGR decreased by 37.5%, from 0.32 to 0.20. The corresponding yield loss during the extraction was in the range of 7.0% to 9.7% (**Table I**), which is in accordance with the results given in a previously published laboratory scale study [10]. The XGR shows a slight decrease over the period of 5-45 min, while the yield loss shows a decrease during this same interval. This might indicate that some xylan redeposition was taking place during the extraction or the Büchner washing procedure used in separation of the filtrates. However, the XGR results indicate that practically the same amount of xylan can be extracted in 5 min as in 60 min. A similar effect has been observed when attempting to upgrade paper-grade pulps to dissolving-grade pulps; the decrease in xylan content during the extraction with sodium hydroxide [27] or nitren [28] occurs very rapidly.

Our hypothesis concerning the negligible effect of extraction time on xylan removal is further supported by the determination of the TOC of the extraction filtrates (**Figure 2**). The slight increase in TOC during extraction could be attributable to some cellulose degradation taking place during extraction.

Extraction Time (min)	Yield Loss (% o.d. pulp)
5	9.7
10	7.3
20	7.0
30	7.4
45	7.8
60	8.1

1. The effect of extraction time (5-60 min) on the yield loss with basis of o.d. pulp.

The TOC content of the filtrate from the pressure-fed screen was somewhat higher than that of the Büchner filtrates. This can be attributed, at least partially, to the presence of some fines in filtrate from the pressure-fed screen.

In the filtrate sample taken after 60 min of extraction time, TOC content was 1.06 g/L. We presume that all of this TOC originates from the extracted xylan, and that it would correspond to 63.1 kg of xylan, representing 9.5% of the pulp material and 38.1% of the xylan in this pulp. Both of these values are in good agreement with the results from the determination of pulp XGR and yield loss. Thus, it seems that the TOC determination used in this study, where pH adjustment is required, is able to give a reliable approximation on the extraction result. These results indicate that a minimum amount of xylan is precipitated during the pH adjustment.

Effect of alkaline extraction and washing on fiber characteristics

Table II shows the WRV, pulp viscosity, and fiber characteristics of the pulp samples determined with the optical fiber analyzer. Modern automated optical analyzers allow measurements to be performed on a good quantity of fibers to give reliable and repeatable results on morphological character of fibers [29]. The alkaline extraction had slight effects on the morphological character of the fibers. First, the average length-weighted fiber length reduced from 0.99 mm to 0.97 mm during the alkaline extraction. Second, the fiber width seems to increase during the alkaline extraction, which is caused by the opening of the inter- and intramolecular structure of the cellulose that renders the fibers into a more swollen form. Thirdly, the coarseness-to-width ratio was reduced, possibly because of the removal of interstitial material during the extraction and consequential increase in fiber wall porosity. For instance, in alkaline pulping, material dissolution causes the pore volume of the fibers first to increase and then to decrease as a result of the collapse of the pore structure, thus yielding a more compact structure [30]. A similar effect likely occurs at the beginning of alkaline extraction as well, resulting in lower coarseness-to-width ratios after 5 min of extraction compared with other extracted samples. Finally, the alkaline extraction caused slight fiber deformations, which can be seen as an increase in the fiber form alternations in the transverse and longitudinal direction (i.e., curl and kink indices).

EXTRACTION

Extraction Time (min)	Water Retention Value (g/g)	Fiber Length ^a (mm)	Fiber Width (μm)	Fines ^a (%)	Coarseness-to-Width Ratio (g/m ²)	Curl (%)	Kink Index (1/m)	Viscosity (mL/g)
0	1.17 ± 0.01	0.99	16.00	1.66	7.00	11.2	733	918 ± 13
5	1.41 ± 0.01	0.98	16.03	1.65	4.43	11.3	728	926 ± 13
10	1.38 ± 0.01	0.97	16.09	1.65	6.06	11.3	780	1024 ± 68
20	1.40 ± 0.01	0.98	16.10	1.62	5.90	11.5	797	1130 ± 32
30	1.41 ± 0.01	0.97	16.14	1.65	5.55	11.8	782	1053 ± 51
45	1.42 ± 0.01	0.97	16.15	1.61	5.76	11.8	810	1134 ± 12
60	1.41 ± 0.01	0.97	16.09	1.65	5.32	11.9	817	967 ± 58
60 + washed	1.35 ± 0.01	0.97	16.65	0.38	5.98	16.4	1429	1032 ± 9
Change caused by pulp washing with MicraScreen, %	-4	±0	+4	-77	+12	+38	+75	+7

^a Length-weighted average.

II. The effect of extraction time and subsequent washing on pulp and fiber properties. The change caused by pulp washing with MicraScreen was calculated as the percentage increase/decrease of the 60 min + washed value compared with the 60 min value.

WRV and pulp viscosity both are affected by the alkaline extraction. WRV increased approximately 20% compared with the reference during the first 5 min of extraction, after which the WRV remained at the same level. Alkali treatment increases the WRV of the pulp, and the results obtained here indicate that the penetration of alkali into the fiber cell wall takes place almost instantaneously, which is in accordance with previous studies [31]. As shown in Table II, the pulp viscosity reaches a maximum value over 20 min to 45 min. At the initial extraction, there is practically no influence on pulp viscosity, although some hemicelluloses can be extracted. However, this is interesting since it reveals that the process could be intensified but that the process conditions (e.g., extraction time) are very crucial in terms of end product quality. For instance, a small change in the delay time during the extraction from 5 min to 10 min apparently would change the pulp viscosity more than 10%. The degree of polymerization is substantially lower for hemicelluloses in comparison to cellulose. In this context, it seems reasonable that the increase in pulp viscosity at the beginning of the extraction is at least partially attributable to the lower content of hemicelluloses in the pulp samples. However, the pulp viscosity decreased toward the end of the extraction, although no changes in xylan content were observed. Consequently, we can assume that, because all of the removable xylan has been extracted, change in the cellulose form, shifts in the arrangement of cellulose agglomerates, or a decrease in the degree of polymerization of cellulose might occur [32,33].

The amount of primary fines remains at a nearly constant level during alkaline extraction. The modest changes in the fines content of the pulp samples can be explained by some losses taking place in the Büchner filtration of the pulp sam-

ples. However, the pulp fines contents given in Table II reveal that the MicraScreen equipment used for pulp washing fractionated the extracted pulp heavily. As a result of the washing procedure, the pulp fines content was reduced from about 1.7% to 0.4%. Because the loss of fines is clearly undesirable, some other arrangements in pulp washing should be considered to preserve the primary fines in the pulp.

Although the pulp fines content was substantially reduced by the washing procedure, the WRV was reduced by only 4%. Thus, we can conclude that the primary fines do not contribute significantly to the WRV in this case, and that the increase in WRV mainly was the result of an altered fiber structure. Normally, the fines fraction of chemical pulp has a high content of ionic groups, which contributes positively to the water-binding capacity of the pulp [34,35]. However, according to our previous results [36], the fines separated from alkali-extracted birch kraft pulp contain notably less of these ionic groups than the fines from unextracted pulp. Therefore, the water-binding capacity of primary fines probably has been reduced by alkaline extraction.

Hemicelluloses are the primary source of ionic groups in chemical pulp. Thus, the WRV can be expected to decrease when the hemicelluloses are partially removed. However, our results indicate that a 20.5% increase in pulp WRV can be observed during the first 5 min of extraction, after which the WRV remains quite stable. Because the WRV increased despite the partial removal of hemicelluloses, we presume that the alkaline extraction used here mainly removed xylan from the fiber surfaces. For ECF-bleached birch kraft pulp fibers, it has been reported that the surface layer has a higher relative content of xylan in comparison with the inner layers [37]. When the surface xylan is removed, more of the charged

EXTRACTION

Property	0 min	5 min	10 min	20 min	30 min	45 min	60 min	60 min + washed	Change Caused by Pulp Washing with MicraScreen, %
Apparent bulk-density, kg/m ³	679	690	694	693	691	689	684	675	-1
°SR, -	21	20	20	20	20	20	20	17	-15
Tensile index, Nm/g	42.5 ± 3.0	42.0 ± 1.3	43.1 ± 2.5	41.6 ± 1.1	42.1 ± 1.1	39.7 ± 1.7	41.2 ± 1.9	35.1 ± 1.5	-15
Tear index, Nm ² /kg	7.44 ± 0.47	7.99 ± 0.36	8.22 ± 0.22	7.38 ± 0.42	7.91 ± 0.33	7.00 ± 0.55	6.86 ± 0.45	6.58 ± 0.22	-4
Tensile stiffness index, kNm/g	6.28 ± 0.20	6.53 ± 0.20	6.59 ± 0.28	6.24 ± 0.22	6.48 ± 0.17	6.32 ± 0.17	6.36 ± 0.29	5.6 ± 0.24	-12
Stretch, %	2.46 ± 0.31	2.31 ± 0.09	2.43 ± 0.24	2.60 ± 0.18	2.48 ± 0.17	2.30 ± 0.18	2.57 ± 0.23	2.40 ± 0.13	-7
Tensile energy absorption index, mJ/g	765.7 ± 136.8	720.2 ± 43.6	778.1 ± 111.6	799.6 ± 52.3	777.6 ± 66.0	678.8 ± 76.1	786.5 ± 86.8	626.7 ± 46.3	-21
Air permeance (Bendtsen), µm/Pas	35.3 ± 2.7	34.5 ± 0.8	32.6 ± 0.7	33.8 ± 1.4	35.1 ± 1.0	35.0 ± 0.9	33.4 ± 2.4	40.4 ± 0.0	+20
Light-scattering co-efficient, -	32.4	33.2	32.2	33.1	32.7	32.8	32.9	31.6	-4
Opacity, -	75.4 ± 0.34	76.2 ± 0.36	75.4 ± 0.67	75.9 ± 0.75	75.6 ± 0.38	75.7 ± 0.45	75.7 ± 0.57	75.4 ± 1.28	±0

III. The paper properties of handsheets made from extracted pulp samples. The change caused by pulp washing with MicraScreen was calculated as the percentage increase/decrease of the 60 min + washing value compared to the 60 min value.

groups in the fiber wall are exposed, allowing more water to penetrate the fiber wall. In addition, the more porous structure of the fiber wall would lead to increased accessibility of the remaining charged groups in the fiber wall. Water is much harder to remove from intra- than inter-wall locations [38]. Therefore, we can conclude that the location of the hemicelluloses remaining within the porous fiber wall after extraction plays an important role in determining the water binding capacity of the extracted fibers.

The washing procedure caused a 38% increase in fiber curl and a 75% increase in the kink index. The notably higher increase in the kink index indicates that the shear forces generated by pumps and other equipment mainly induce clearly measurable angles (kinks) in the three-dimensional fiber shape rather than merely curling the fibers. This finding is in line with the fact that fibers with a low amount of hemicelluloses are very susceptible to mechanically induced deformation and acquire more local fiber wall defects compared with pulp with a high hemicellulose content [39-41].

Effect of alkaline extraction and washing on paper properties

Table III shows the properties of handsheets made from non-beaten pulps. The results indicate that a shorter

extraction time would be more favorable in terms of the paper properties of non-beaten pulp. The washing procedure used here and the resulting removal of primary fines had a detrimental effect on the strength properties of non-beaten pulp. Before preparation of the handsheets, the reference sample (0 min extraction) needed to be wet-disintegrated according to ISO 5263-1:2004, "Laboratory wet disintegration -- Part 1: Disintegration of chemical pulps," to remove fiber bundles. Alkaline extraction was found to remove fiber bundles, so the wet-disintegration procedure was not required for the extracted samples. This observation indicates that if alkaline extraction is performed for baled birch pulp, subsequent deflaking of the pulp is not needed after slushing and extraction.

Table III demonstrates that paper properties such as tensile, tear, and tensile stiffness indices increase at the beginning of extraction and decrease toward the end of extraction. Despite the slight increase in the initial paper properties at the beginning of alkaline extraction, development of paper properties during beating is slower for pulp with low hemicellulose content [31,42]. Therefore, the beatability of alkaline extracted pulp samples likely deteriorated to some extent with shorter extraction times.

EXTRACTION

CONCLUSIONS

We demonstrated a pilot-scale alkaline extraction trial using 0.56 M sodium hydroxide to remove xylan from birch kraft pulp fibers. The effect of the extraction time on the carbohydrate composition of the pulp, and on the fiber and paper properties, shows the following:

- Alkaline extraction time has no effect on xylan removal; a similar amount is extracted in 5 min as in 60 min.
- Alkaline extraction of 60 min has only modest effects on fiber morphology. However, a 20% increase in WRV occurs during the first 5 min of extraction.
- Shorter extraction times are beneficial for the paper properties of non-beaten pulp, which indicates an opportunity for process intensification.

The scale-up of the alkaline extraction procedure for bleached birch kraft pulp is possible, although the pulp washing procedure used in our study revealed that the removal of sodium hydroxide from the pulp requires optimization. In our case, the alkaline-extracted fibers were damaged during washing and the primary fines were almost completely lost. In addition, if the xylan-rich alkaline filtrates are not used as such at the mill, the efficient recovery of xylan from the alkaline filtrates and reuse of sodium hydroxide in extraction is an important aspect for the economy of the process. Therefore, developments in separation processes are needed for achieving feasible recovery of the extracted xylan. However, the alkaline extraction of xylan from bleached birch kraft pulp could offer a new specialty fiber to be used as a platform material for fiber engineering and pure polymeric xylan with potential use in high value products. **TJ**

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EXTRACTION

ABOUT THE AUTHORS

Alkaline extraction previously has been investigated when attempting to convert paper-grade kraft pulps to dissolving-grade pulps. However, after extracting the fibers at milder alkaline conditions, the hemicellulose extracted kraft pulp fibers possibly could be used as a functional fiber component in the papermaking furnish. Therefore, we have chosen this topic to give new insights into the effects of alkaline extraction on fiber and paper properties. The present study focuses on alkaline extraction of bleached birch kraft pulp with particular attention to the effect of extraction time on xylan dissolution.

The most interesting finding obtained from this study was that alkaline extraction time has no significant effect on the quantities of xylan removal; a similar amount was extracted in 5 min and in 60 min, respectively. Also, shorter extraction times are beneficial for the paper and fiber properties of non-beaten pulp. Therefore, the extraction of xylan could be considered to be relatively easy to implement in an industrial scale when short extraction times are required.

The xylan-extracted pulp possibly could be used as a specialty fiber in a variety of applications or as a component in paper or board, whereas the produced



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xylan could be used in-house or sold for product upgrading. This kind of approach could entail process intensification opportunities or new sources of revenue for pulp and paper industry companies.

The next step in our research is to study the effects of the addition of xylan-poor fibers in the papermaking process on wet-end chemistry and end-product properties.

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PUBLICATION IV

Surface selective removal of xylan from refined never-dried birch kraft pulp

Saukkonen, E., Lyytikäinen, K., Geydt, P. and Backfolk, K.

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Surface selective removal of xylan from refined never-dried birch kraft pulp

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Abstract In this study, the effect of enzyme treatment on refined, never-dried bleached birch kraft pulp was investigated, using an endo-1,4- β -xylanase, that is substantially free from cellulase activity. The xylanase treatment of refined never-dried pulp revealed a rapid initial hydrolysis rate with a time-dependent saturation level in the amount of hydrolyzed pulp carbohydrates. Surprisingly short xylanase treatment times were found to have an impact on the fiber surface structure and on the physicochemical properties of kraft pulp fibers. Xylanase treatment led to mild microscopic differences in the ultrastructure of a never-dried fiber, whereas local topographical differences were distinguishable with atomic force microscopy. Results from the analysis of dissolved carbohydrates and the

interfacial properties of the xylanase-treated never-dried fibers thus confirm a selective removal of xylan from the fiber surfaces. The zeta-potential charge and dewatering properties of the pulp slurry, fiber morphology, and strength properties of the paper were affected, which is a concomitant of xylanase treatment. However, the papermaking properties of the fibers were mainly preserved with simultaneous improvement in the dewatering rate of the pulp. Thus, optimized xylanase treatment of refined bleached kraft pulp provides a fiber for papermaking or fiber modification purposes with a selectively modified chemical composition of the fiber surface layer.

Keywords Atomic force microscopy · Birch kraft pulp · Fiber surface · Never-dried · Topography · Xylanase

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Introduction

Growing interest in the utilization of lignocellulosic biomass has led to the development of various biorefinery concepts, wherein one option is the utilization of hemicellulose-rich process streams or integration of hemicellulose extraction concepts to an existing kraft pulp mill (Christopher 2012). Several options for the extraction of xylan from the kraft pulp mill material streams have been proposed; from wood chips prior to cooking by a prehydrolysis process

(Chirat et al. 2012; Testova et al. 2011), near-neutral (Lundberg et al. 2012; Mao et al. 2008), or alkaline extraction (Al-Dajani and Tschirner 2008; Helmerius et al. 2010), from early cooking liquor (Axelsson et al. 1962; Axegard et al. 2009), from weak black liquor (Axelsson et al. 1962; Öhman and Danielsson 2011), from LignoBoost filtrates (Wallmo et al. 2009), or even from bleached hardwood kraft pulp by alkaline extraction (Fuhrmann and Krogerus 2009; Saukkonen et al. 2012). The extracted xylan fraction could serve as a high-value co-product for various end uses in conjunction with the produced paper-grade kraft pulp (Deutschmann and Dekker 2012).

Upgrading of paper-grade hardwood kraft pulps into dissolving pulps by combining alkaline extraction and enzymatic treatment steps for thorough hemicellulose removal has been done previously (Ibarra et al. 2009, 2010; Köpcke et al. 2010; Gehmayr et al. 2011). However, partial or selective hemicellulose removal from paper-grade hardwood kraft pulp by enzymatic treatment, xylanase treatment in particular, enables tailoring of the papermaking properties of the pulp (Blomstedt et al. 2010). More precisely, the carbohydrate composition of the outermost surface layer of the fibers can be affected by hemicellulases, since these enzymes are active mainly on the fiber surfaces and accessible macropores (Viikari et al. 1994b; Teleman et al. 2001). Recently, Hakala et al. (2013) described thorough xylan removal from hardwood kraft pulp by combining alkaline extraction and xylanase treatment steps to obtain polymeric xylan and xylo-oligosaccharides (XOs) as valuable side streams in dissolving-grade pulp production. XOs are currently produced mainly from agricultural feedstocks rich in xylan but also wood-based raw materials have been considered for XO production (Moure et al. 2006). Compared to xylan-derived biorefining co-products such as xylose for fermentation or polymeric xylan for films, barriers, and hydrogels, XOs could be attractive high-value chemical compounds owing to their pharmaceutical and nutraceutical properties (Aachary and Prapulla 2011). Consequently, XOs could also provide an interesting high-value co-product in a biorefinery concept where selective modification of the carbohydrate composition of bleached hardwood paper-grade pulp rich in xylan is performed by means of hemicellulase enzymes.

Luce (1964) made the first studies on the radial distribution of hemicellulose fractions in fiber walls

and concluded that bleached paper-grade birch kraft pulp fibers have over 30 wt% concentration of xylan in the outermost layers of the fiber. More recently it has been stated that for industrially bleached hardwood kraft fibers the surface xylan concentration can be as high as 40 wt% (Dahlman et al. 2003; Sjöberg 2003). High concentrations of hemicellulose on the surface of paper-grade hardwood kraft pulp fibers have some well-established benefits regarding the papermaking properties of the fibers: beatability (Cottrall 1950; Centola and Borruso 1967; Bhaduri et al. 1995; Silva et al. 2011), bonding potential and strength properties (Rydholm 1967; Schönberg et al. 2001; Hannuksela et al. 2004), and reducing drying-induced hornification (Oksanen et al. 1997b; Köhnke and Gatenholm 2007; Köhnke et al. 2010). When deposited at the outer layer of the fiber, hemicelluloses can act as adhesives or binders to strengthen the bonds between individual fibers in the three-dimensional network of a paper sheet.

However, paper-grade hardwood kraft pulp fibers with high cellulose concentration on the surface layer could serve as a platform material in novel applications for imparting new functionalities to fibers. Technologies such as xyloglucan endotransferase (XET) (Zhou et al. 2006) and the click chemistry of polysaccharides (Liebert et al. 2006) could benefit from pure cellulose surfaces. Pure cellulose surfaces ensure more homogenous reactions (no hemicellulose remnants on the surface to hinder the reactivity of cellulose) and better adsorption of xyloglucan and other polysaccharides (Christiemin et al. 2003; Zhou et al. 2006). The carbohydrate composition of the outermost surface layer of hardwood fibers in particular can be affected by xylanase enzymes that randomly cleave the β -(1,4)-D-xylopyranose backbone of the xylan found in hardwoods (Collins et al. 2005).

The number of studies on fiber modification with cellulases and hemicellulase/cellulase mixtures is vast (Bajpai 2012). Xylanases belong to the group of hemicellulases. The main focus of xylanase utilization in pulp and papermaking has been on bleach boosting (Viikari et al. 1994a; Bajpai 2004) and enhancing the refining of kraft (Noe et al. 1986; Kibblewhite and Clark 1996; Oksanen et al. 1997a; Dickson et al. 2000; Mansfield et al. 2000) or chemi-mechanical pulp (Yang et al. 2011; Lei et al. 2008, 2012). However, there are relatively few publications on the use of xylanases alone in paper-grade pulp fiber modification

where refining energy reduction or bleach boosting is not the main target (Oksanen et al. 2009; Blomstedt et al. 2010). With the exception of Oksanen et al. (2009), there appear to be no studies on the effects of xylanase treatments made on refined never-dried kraft pulps. Furthermore, there is a lack of understanding of the physicochemical state of post-refining xylanase-treated fiber surfaces evaluated in the never-dried state. In addition, hydromechanical and/or enzymatic peeling of the outermost fiber surface layer has been mainly practiced for analytical purposes (Buchert et al. 1996; Ristolainen et al. 2002; Dahlman et al. 2003; Sjöberg 2003; Treimanis et al. 2009), where preservation of the papermaking properties of the fibers is not of high priority.

In this study, refined never-dried birch kraft pulp fibers were treated with an endo-1,4- β -xylanase enzyme solution substantially free from cellulase activity in order to selectively modify the carbohydrate composition of the fibers. Investigations were made on the effect of xylanase treatment time on the physical state of the fibers and removal rate and selectivity of removed chemical components. The particular emphasis of this study is on the state of the never-dried fiber ultrastructure and surface topography, the chemical composition of the dissolved carbohydrates, and maintaining the papermaking properties of xylanase-treated fibers. The selective modification of fiber surface properties with xylanases enables the tailoring of final product properties and could provide valuable co-product streams, such as xylose units and XOs, together with an upgraded surface-purified papermaking fiber with potential use in high-value applications.

Materials and methods

Xylanase treatment

The xylanase enzyme solution used in this study was an endo-1,4- β -xylanase (Shearzyme 500 L, Novozymes A/S, Denmark) with insignificant side activities, produced by *Aspergillus oryzae* which carries the gene-encoding family 10 xylanase from *A. aculeatus*. The xylanase activity was assayed by the 3,5-dinitrosalicylic acid (DNS) method (Miller 1959) using a 1 % solution of beech xylan (Sigma-Aldrich, Germany) as substrate. The activity of the enzyme solution in pH 5 at 50 °C was 59,300 nkat/mL.

Elemental chlorine free (ECF) bleached never-dried birch kraft pulp was obtained from a Finnish pulp mill and used as raw material for the xylanase treatment. In order to activate the fiber surface for better accessibility of xylanase, the pulp was refined to Schopper–Riegler degree (SR°) 24 prior to xylanase treatment, using a pilot-scale disc refiner with a specific energy consumption of 32 kWh/t. Xylanase treatment was performed in a 5-m³ extraction vessel for 165 kg of odw pulp at 50 °C for 90 min with an enzyme dose of 15 kg/t of odw pulp, corresponding to 890 nkat xylanase/g of dry pulp. Prior to xylanase treatment, the pH of the pulp suspension (3.3 % consistency) was adjusted to 5 with a dilute solution of sulfuric acid (H₂SO₄). The xylanase treatment conditions used in this study were selected based on our previous study by Metsämuuronen et al. (2013), in order to achieve a high xylo-oligosaccharide (XO) yield in the dissolved carbohydrates. After 90 min of xylanase treatment, the enzymes were deactivated by heating the pulp suspension from 50 to 90 °C at a rate of 1.0 °C/min and keeping it at that temperature for over 30 min.

In order to remove the denaturated enzyme residues and the dissolved carbohydrates from the stock, the xylanase-treated pulp was dewatered on a pilot paper machine without any chemical dosing. The paper web was dried with air and recovered as a wet lap pulp at a dry matter content of approximately 35 %. A similar procedure was followed for the untreated reference pulp, which was refined to SR° 17 using the pilot-scale disc refiner with a specific energy consumption of 9 kWh/t. The xylanase-treated (**XT pulp**) and reference (**R pulp**) wet lap pulps were reslashed with a wet disintegrator according to standard ISO 5263-1. The pulp preparation procedure is depicted in Fig. 1.

Sampling

Pulp samples were collected from the extraction vessel before xylanase treatment and after 10, 20, 30, 60, and 90 min of treatment time. Immediately after sampling, the pulp samples (66 g odw) were washed with 8 L of hot tap water in order to remove the enzyme residues and dissolved carbohydrates. The washing was performed by filtration using a Büchner funnel equipped with a commercial wire (Tamfelt Gapmaster Pro F35654GM). The first filtrates, approximately 2 L, from each sample were recovered for further

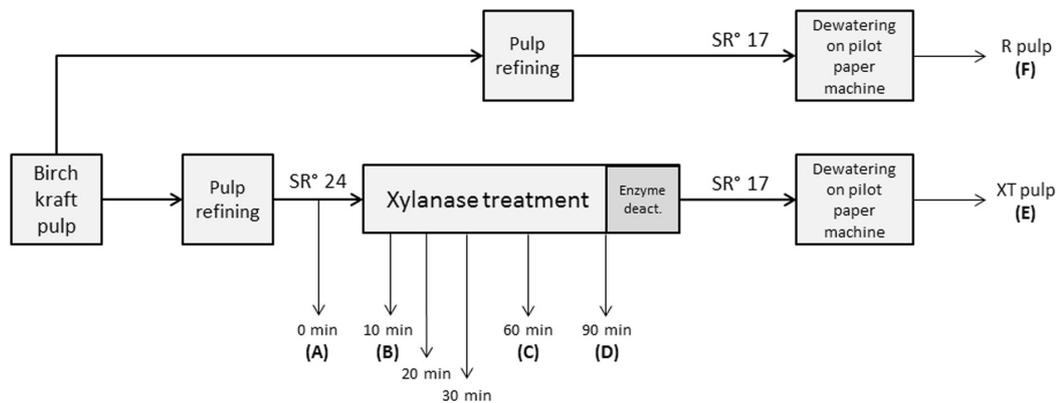


Fig. 1 The pulp preparation procedure and sample (A–F) labeling

investigation. A similar washing procedure was also applied to wet disintegrated XT and R pulp samples. After washing, the pulp cakes were stored in a cold room at a consistency of 1.5 %. The pH of the pulp samples was adjusted to 8 with a dilute solution of sodium hydroxide (NaOH) before storing them.

Carbohydrate analyses

All the carbohydrates (both mono- and oligosaccharides) dissolved in the pulp filtrates by the xylanase treatment were analyzed from the collected first Büchner funnel filtrates as described in Sundberg et al. (1996). The total carbohydrate content quantified as monosaccharide composition was analyzed by gas chromatography HP6890 + injector HP7683 (Agilent, USA). The column was a 25 m/0.20 mm i.d. wide-bore capillary column with a nonpolar phase (HP-1, Agilent Technologies) having a film thickness of 0.11 μm . The amount of xylo-oligosaccharides from the dissolved carbohydrates was not studied in detail within this study.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

SEM and AFM images were taken to determine the microscopic ultrastructure, nano-scale topography, and physicochemical properties of the fiber surfaces. Samples for SEM and AFM imaging were prepared with a British handsheet mold. Handsheets with a

grammage of 60 g/m^2 were gently wet-pressed to an approximate dry matter content of 25 % and stored in a cold room in this ‘semi-wet state’. This was done in order to preserve the never-dried state of the fibers by preventing drying-induced hornification (Weise 1998). The sample preparation technique adopted prior to both SEM and AFM characterization was rapid freezing (cryofixation) of the semi-wet handsheets in liquid nitrogen (N_2), followed by overnight freeze-drying. This procedure was inspired by earlier work that studied the ultrastructure of kraft pulp fibers in the never-dried state by SEM (Daniel and Duchesne 1998; Duchesne et al. 2001) and interfacial properties by AFM measurements (Fahlén 2005). The fiber morphology and the overall physical character of the fiber ultrastructure were evaluated by SEM: JEOL 5800 SEM (JEOL, USA) with a 15 kV accelerating voltage and a 10 mm working distance.

Atomic force microscope (AFM) imaging was used to characterize the changes in the nano-scale structure, topography, and interfacial properties of the bleached birch kraft pulp fibers before and after xylanase treatment. AFM measurements were made (BRUKER Multimode 8 Scanning Probe Microscope, Bruker, USA) in tapping mode. A low spring constant ($k = 5 \text{ N/m}$) and probe containing an Al-covered Si surface with a typical resonant frequency of 150 kHz and tip radius of $<8 \text{ nm}$ were used. AFM images were captured on areas of $2 \times 2 \mu\text{m}$ having no rapid vertical drops over 200 nm in order to have a minimal amount of defects and artifacts in the images. Root mean squared (RMS) surface roughness values were

determined for $2 \times 2 \mu\text{m}$ scanned surfaces and for five different areas of each sample.

Pulp testing

The pulp water retention value (WRV), wet zero-span tensile strength (WZST), and SR° number were determined according to standard methods: ISO 23714, ISO 15361, and SCAN-C 19:65, respectively. Fiber properties such as the kink index, fiber length and width were determined using an optical fiber analyzer (Lorentzen & Wettre, Sweden), and the zeta potential of the fiber suspension was determined using a Müttek SZP-06 device (BTG, Switzerland). To evaluate the theoretical amount of surface xylan (wt%) in the fibers, the cell wall thickness (CWT) of the non-refined fibers was determined using a Kajaani FiberLab optical fiber analyzer (Metso, Finland). The preparation of handsheets and testing of paper properties were performed according to EN ISO 5269-1:1998 from pure pulp samples without any addition of chemicals.

Results and discussion

Dissolved carbohydrates from the fibers

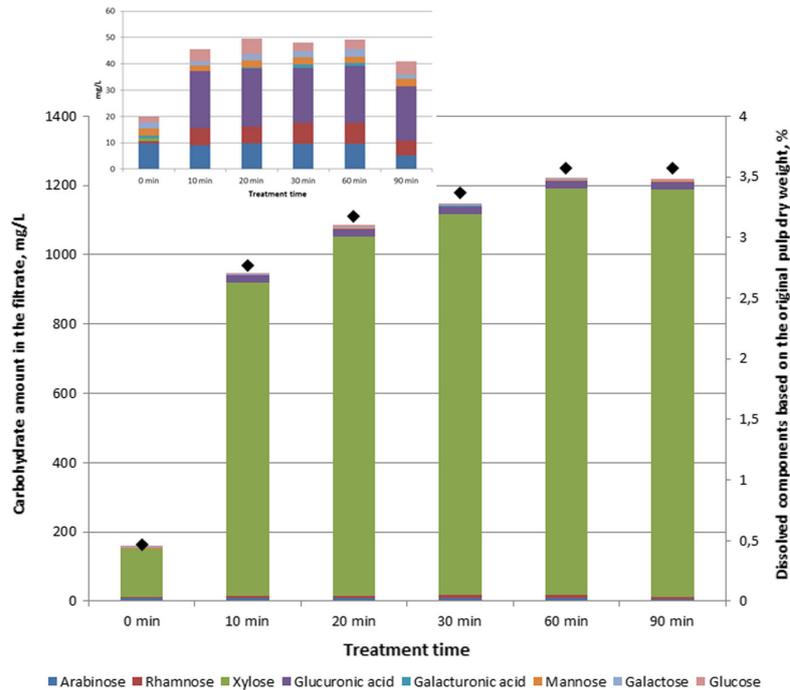
The xylanase treatment dissolved carbohydrates from the fiber material (Fig. 2). The reference sample (0 min) contained small amounts (160 mg/L, corresponding to 0.47 wt% of odw pulp) of dissolved carbohydrates. This is in accordance with the literature, concerning carbohydrates which are dissolved during birch kraft pulp refining (Lindström et al. 1978). Figure 2 shows that a somewhat similar amount of xylan can be dissolved in 10 min, as the amount obtained after 90 min of xylanase treatment, i.e. 2.8 wt% (10 min) and 3.6 wt% (90 min) of the original pulp dry weight was hydrolyzed. In addition, the amount of rhamnose and glucuronic acid released was found to be 6.6 and 21.6 mg/L, respectively, after 10 min of xylanase treatment, after which their content in the pulp filtrate did not increase (Fig. 2, top left histogram). Thus, these side group residues bound to the birch xylan backbone were subjected to a rapid initial hydrolytic attack by the xylanase enzyme. Furthermore, the amount of carbohydrate components, apart from xylose, in the pulp filtrates decreased from

49.3 to 40.9 mg/L between 60 and 90 min of xylanase treatment. This suggests that reprecipitation of the released hydrolysis products might occur after 60 min of xylanase treatment.

Oliveira et al. (2012) improved the rate and extent of the xylan hydrolysis of bleached eucalyptus kraft pulp with xylanase by applying a robust ultrahigh hydrostatic pressure (UHP) treatment to the pulp prior to enzymatic hydrolysis. By increasing the enzyme-accessible surface area, the hydrolysis rate of xylan by xylanase can be increased. The low consistency refining of chemical pulp used in this study is, thus, likely to have contributed to the high xylan hydrolysis rate during the initial stages of the xylanase treatment. A reduction in the xylanase hydrolysis rate was observed in this study similar to that reported by Oliveira et al. (2012) for 75-min xylanase treatment of bleached eucalyptus pulp. It is probable that the reaction rate of enzymatic hydrolysis is restricted by the accumulation of reaction product, superficially adsorbed excess xylanase, and the thorough removal of easily accessible xylan from the outermost fiber surface layer of the bleached birch kraft pulp.

The predominant part (96.7 wt%) of the total amount of dissolved carbohydrates during the xylanase treatment of bleached birch kraft pulp was xylose derived from the β -(1,4)-D-xylopyranose backbone of xylan. Together with the 0.5 wt% rhamnose and 1.7 wt% glucuronic acid in the pulp filtrates, the amount of xylan-derived compounds can be estimated to be over 98.5 wt%, after 90 min of xylanase treatment. Therefore, the 3.6 wt% of the original pulp dry weight dissolved after 90 min of xylanase treatment corresponds to 14.2 wt% of the total amount of xylan, calculated from the 24.9 % xylan content in bleached birch kraft pulp (determined for the same raw material in our previous work (Saukkonen et al. 2012). Based on a theoretical evaluation, the xylan content that is located in the outermost fiber layers, i.e. the primary cell wall (P) and outer secondary cell wall layer (S_1), of the bleached birch kraft pulp fibers used in this study is approximately 15 wt% ([link to supplementary material](#)). Thus, these results demonstrate that the commercial xylanase solution substantially free from cellulase activity is very specific and can be used in the selective removal of surface xylan from the outermost fiber layers of refined never-dried bleached birch kraft pulp. The ratio of mono- and oligosaccharides was not studied in detail within this

Fig. 2 Amounts of all pulp carbohydrate components (mg/L) dissolved during xylanase treatment as a function of time and dry weight yield loss (filled diamonds) based on the original pulp dry weight. The amounts of carbohydrate components apart from xylose are illustrated in the top left histogram



study. However, according to Metsämuuronen et al. (2013), bleached birch kraft pulp treated with endo-1,4- β -xylanase (Shearzyme 500 L) in similar conditions releases xylo-oligosaccharides (XOs), particularly xylobiose and xylotriose, at moderately high concentrations, whereas the proportion of xylose in the dissolved carbohydrates is small.

Fiber ultrastructure

Changes in the surface morphology of hardwood kraft pulp fiber in the form of cracks, flakes, filaments and the formation of external fibrillation are known to occur during ECF bleaching with xylanase treatment (Garg et al. 1998; Torres et al. 2000; Roncero et al. 2005). However, Moss and Pere (2006) reported that no significant differences in the fiber surface morphology were observed between the reference sample and after 2–48 h xylanase treatment of bleached non-refined pulp, when characterized by environmental SEM. Contrary to the study by Moss and Pere (2006), the cryofixation/freeze-drying procedure used in this study enabled us to observe changes in the surface ultrastructure of the fibers prior to drying-induced

hornification. The hornification-inhibitive drying procedure suggests that xylanase treatment induces micro-scale changes in the fiber ultrastructure and topography in the never-dried state (Fig. 3). Salmén and Burgert (2009) state that the secondary cell wall layers (S_1 , S_2 , S_3) can be distinguished from the inclinations of the parallel-oriented cellulose fibrils with respect to the cell axis (cellulose microfibril angle, MFA); an outer S_1 having a transversely oriented, S_2 an axially oriented and an inner S_3 also with transversely oriented fibrils. The striated surface structure and formation of mild external fibrillation gives an indication of the process of peeling of the outermost fiber surface layer of xylanase-treated samples B, C, D, and E. Especially, after 60- (sample C) and 90-min (sample D) of xylanase treatment, the secondary cell wall (S_2) layer microfibril strands aligned parallel to the fiber axis are more visible compared to untreated samples A (0 min) and F (R pulp). This implies that some removal of the primary cell wall (P) layer, which has a criss cross microfibril orientation, has taken place, as well as some removal of the outer secondary cell wall (S_1) layer, which has a transverse microfibril angle to the longitudinal

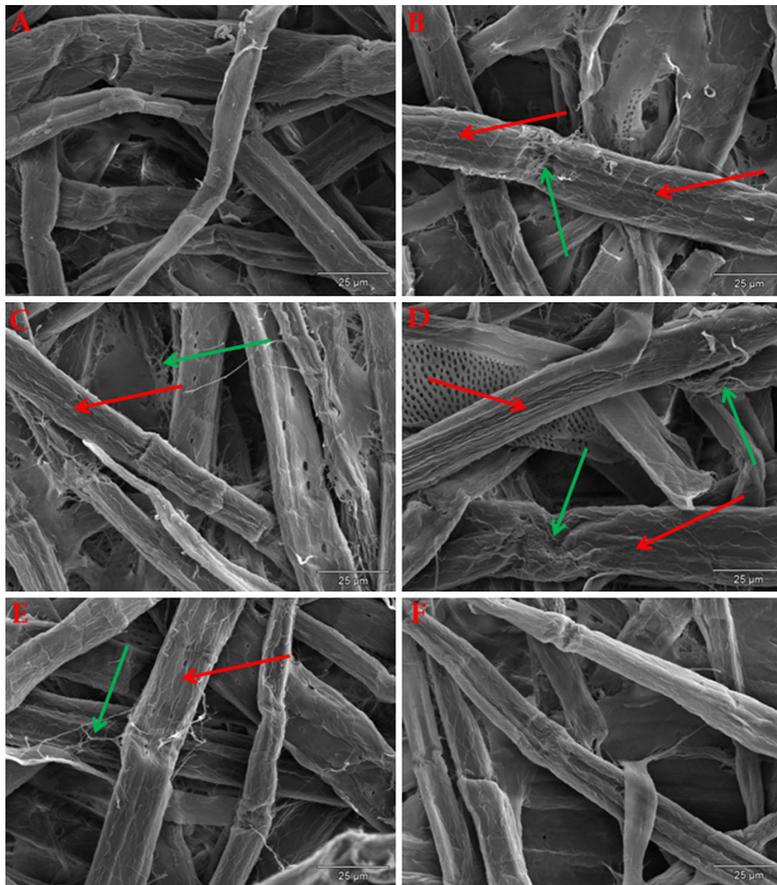


Fig. 3 SEM images of birch kraft handsheets (dried with cryofixation/freeze-drying procedure) after different xylanase treatment times: **a** 0 min, **b** 10 min, **c** 60 min, **d** 90 min, **e** XT pulp, and **f** R pulp. The *red arrows* indicate the microfibril

strands of the secondary cell wall (S_2) layer aligned parallel to the fiber axis. The *green arrows* indicate the formation of mild external fibrillation

direction of the fiber. However, the changes seen in the fiber ultrastructure and morphology caused by xylanase treatment after pulp refining are minor compared to the extent of differences seen in the SEM images of pulp fibers bleached with xylanase treatment obtained by Garg et al. (1998), Torres et al. (2000), and Roncero et al. (2005).

Interfacial properties of the fibers

The nano-scale fiber surface structures determined by AFM presented in Fig. 4 confirm the changes taking

place in the never-dried fiber surface layer. The relatively smooth surface appearance present in sample A (0 min) gradually disappears during xylanase treatment. These images imply that xylanase treatment is very surface-specific and that the xylose-based residues in the pulp filtrates have been released mainly from the fiber surfaces. This can be ascribed to the fact that the cellulose microfibrils aligned parallel to the fiber axis on the fiber surfaces become more visible in AFM images during xylanase treatment. Especially, after 60- (sample C) and 90-min (sample D) treatment times, the aligned surface microfibrils are clearly

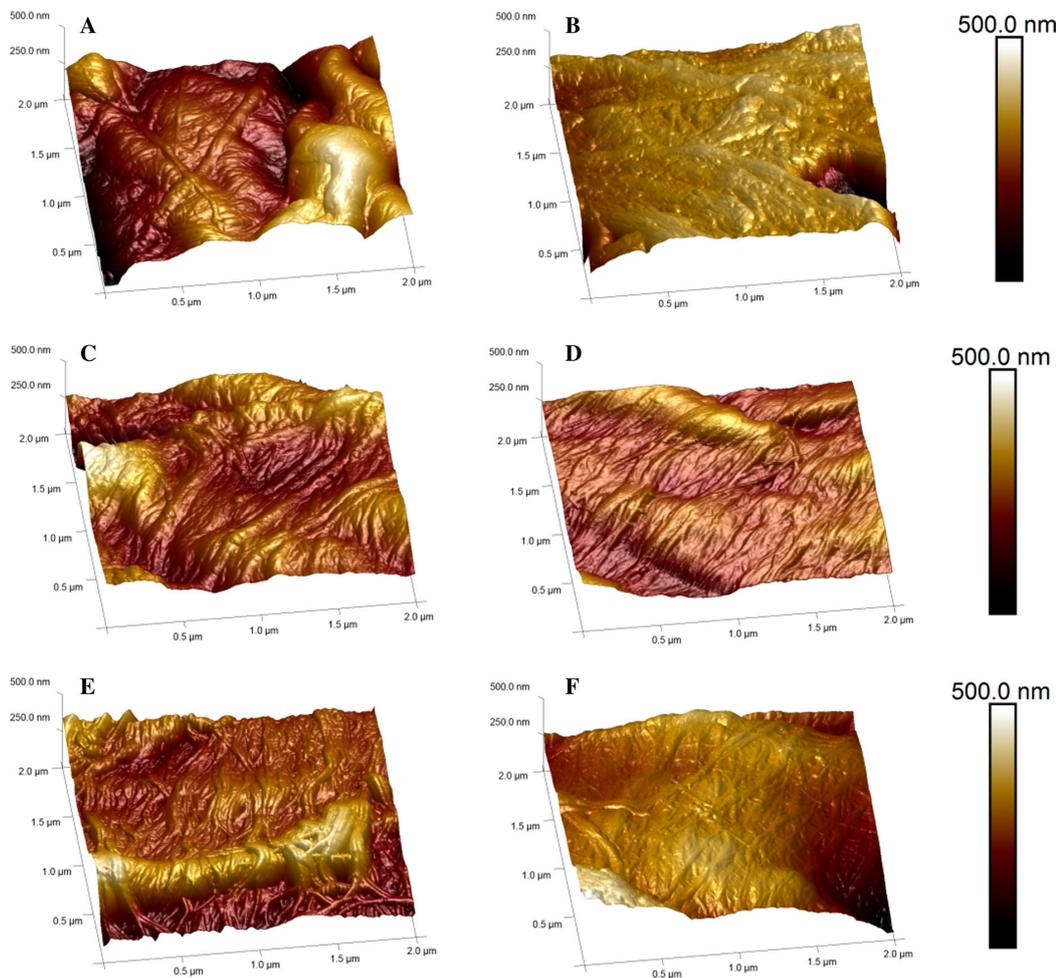


Fig. 4 AFM images of 3D fiber topography (scan size $2\ \mu\text{m} \times 2\ \mu\text{m}$) of birch kraft handsheets after different xylanase treatment times: **a** 0 min, **b** 10 min, **c** 60 min, **d** 90 min, **e** XT pulp, and **f** R pulp

distinguishable from the 3D topography images. Hence, the S_2 -layer of the fiber has been exposed as the surface fibrils are parallel to the fiber direction. These findings are in agreement with studies made by Viikari et al. (1994b) and Teleman et al. (2001) who have reported that xylanase is active mainly on the pulp surface and on the accessible surface macropores in the fiber cell wall. Partial xylan removal from bleached birch kraft pulp with a mild NaOH solution have also shown changes in the fiber surface structure

observed by AFM measurement of freeze-dried fibers (Lyytikäinen et al. 2014).

According to Mironov (2004), the local stiffness of the material has an essential influence on the amplitude and phase, due to changes in the force gradient between the sample and the cantilever. Interestingly, after 10 min of xylanase treatment (sample B), there seems to be an intermediate phase in xylan liberation from the fiber surfaces presented as an irregular surface pattern, seen especially in the phase and

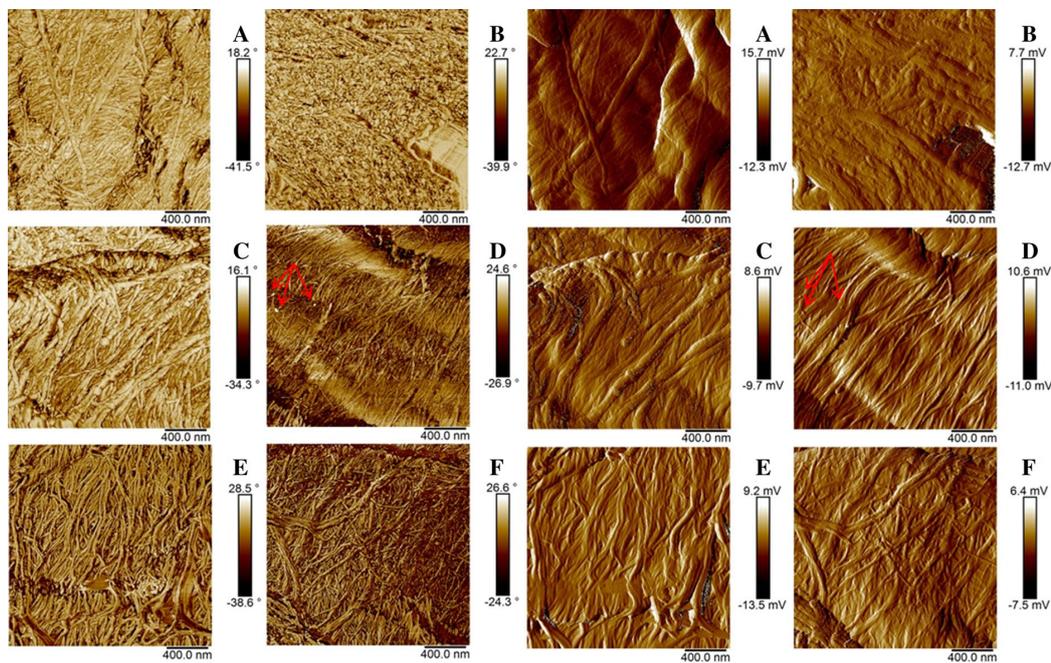


Fig. 5 Phase (*left*) and amplitude (*right*) AFM images on the fibers (scan size $2\ \mu\text{m} \times 2\ \mu\text{m}$) of birch kraft handsheets after different xylanase treatment times: **a** 0 min, **b** 10 min, **c** 60 min,

d 90 min, **e** XT pulp, and **f** R pulp. *Red arrows* indicate possibly reprecipitated particles

amplitude image in Fig. 5. However, Carrillo et al. (2005) assumed that in the initial stages of enzymatic hydrolysis with cellulase enzyme, the adsorbed enzymes might form a layer on the surface of the substrate, and the excess of the enzyme would be adsorbed, forming additional layers. Thus, it is postulated that at the beginning of xylanase treatment (sample B), the residues of the surface xylan create a partially hydrolyzed xylan layer together with the superficially adsorbed xylanase enzyme. As the action of xylanase and the xylan removal process proceed, the oriented microfibrils become detectable from both the 3D topographies (Fig. 4) and the phase/amplitude images (Fig. 5). The possible reprecipitation of the dissolved carbohydrates after 60 min of xylanase treatment has been suggested based on the amount of carbohydrates in the filtrates (Fig. 2). The white dots and protuberances, a few tens of nanometers in size, that frequently appear in the phase and amplitude images, respectively, of the sample D (90 min) surface could represent reprecipitated carbohydrate

aggregates or self-assembled structures. However, the composition and origin of these nano-sized particles should be verified with further studies. While the SEM images show only minor differences in the micro-scale ultrastructure of the XT and R pulp fibers, both the nano-scale 3D surface topography (Fig. 4) and the interfacial properties (Fig. 5) of these samples reveal changes in the superficial structure of the fibers. The fibrillar surface structure of the R pulp (sample F) shows no clear orientation of fibrils in the phase and amplitude images, whereas the fibrillar surface structure in the XT pulp (sample E) has a similar fibril orientation as sample D (90 min). Thus, the xylanase treatment applied in this study causes changes in the nano-scale material properties, rather than inducing clearly detectable microscopic ultrastructural changes.

The results shown in Table 1 further reflect some physical interfacial modification of the fibers associated with the action of xylanase on refined never-dried bleached birch kraft pulp and the removal of surface xylan in particular. Ristolainen et al. (2002) suggested

Table 1 Average roughness (RA) and RMS roughness values for xylanase-treated samples (standard deviation given in

	0 min	10 min	20 min	30 min	60 min	90 min	XT pulp	R pulp
RA (nm)	45 (4)	25 (3)	39 (5)	25 (8)	38 (4)	75 (21)	38 (10)	42 (7)
RMS (nm)	53 (3)	33 (6)	51 (7)	32 (9)	48 (5)	93 (26)	50 (11)	52 (9)

that together with the chemical changes in the fiber surface, some structural and physical changes take place as a function of the xylanase treatment time of bleached birch kraft pulp. It appears that in our case, the initial xylanase treatment has decreased the nano-scale surface roughness due to the removal of surface xylan. Han et al. (2012) and Silva et al. (2011) have reported that the distribution of adsorbed xylan on the surface of hardwood kraft pulp fibers roughens the 3D topography of fiber, observed using AFM. Thus, the initial decrease in RMS values can be related to the removal of surface xylan, whereas after 90 min of xylanase treatment, the increase in surface roughness may be due to a change in the ultrastructure of the fiber cell wall. In a recent review, Pönni et al. (2012) reported that the removal of hemicelluloses leads to cellulose fibril aggregation, i.e. nano-scale coalescence in never-dried fibers. Consequently, the observed increase in RMS could indicate some nano-scale cellulose coalescence taking place on the fiber surface caused by the prolonged 90-min xylanase treatment. However, the roughness values were on a similar level for both untreated (R pulp) and xylanase-treated (XT pulp) pulps. This implies that, whereas differences are distinguishable in the other ultrastructural and interfacial features presented in Figs. 3, 4, 5, the differences in nano-scale surface roughness can be observed by comparing completely never-dried samples (A–D) rather than wet lap pulp samples (E and F) air-dried on pilot paper machine to a dry matter content of approximately 35 %.

Fiber and papermaking properties

Xylanase treatment increased the dewatering rate of the pulp and caused changes in the fiber morphology with a slight decrease in fiber length and increase in clearly measurable angles (kinks) in the 3D fiber shape (Table 2). The SR number decreased from 24 to 17 as xylanase acted on the fiber surface, removing water-binding xylan. In addition, the xylanase may have acted preferentially on the high surface area fines fraction which has a propensity to hinder dewatering

by blocking interstices in the fiber network. Blomstedt et al. (2010) and Oksanen et al. (2009) also reported improved dewatering properties of xylanase-treated bleached hardwood kraft pulp. WRV decreased from 212 to 195 % during 90-min xylanase treatment, which is in accordance with the studies reported by Oksanen et al. (1997b) and Moss and Pere (2006) on the xylanase treatment of non-refined never-dried bleached kraft pulp. Both the decreased SR number and WRV give rise to a dryness level that is achieved after the wire section and wet pressing unit of the paper machine. Thus, the initial wet web strength (IWWS) expectation for post-refining xylanase-treated pulp is high, owing to the fact that paper web dryness has a major positive impact on IWWS (Belle et al. 2014).

Du et al. (2012) have shown that the negative electrical charge of the fiber suspension measured as zeta potential value increases when bleached softwood pulp is xylanase-treated before refining. A similar decrease in zeta potential, but to a greater extent is observed in this study when xylanase treatment is applied after refining. In addition, the rapid increase in zeta potential value determined for the fiber suspension is seen after as little as 10 min of xylanase treatment as the zeta potential value increases from -81.0 to -64.2 mV. The 4-*O*-methylglucuronic acid side groups bound to the xylan backbone are known to increase the anionic charge of the bleached birch kraft pulp fibers substantially (Sjöström 1989). The amount of glucuronic acid released was 21.6 mg/L after 10 min of xylanase treatment and, thus, the decreasing fiber charge can be attributed to the removal of the anionic side groups present in the surface xylan of the fiber and fines. This finding further demonstrates that the xylanase solution used has a high hydrolytic activity on glucuronic acid-branched xylan (glucuronoxylan) found in hardwoods. The difference in zeta potential was seen to a smaller extent between untreated (R pulp) and xylanase-treated (XT pulp) pulp. This was, however, expected as the R pulp was refined to the same SR number as the XT pulp.

The concomitant deterioration of fiber strength properties has often been observed with cellulase

Table 2 Effect of xylanase treatment time on fiber and paper properties (standard deviation given in brackets)

Fiber property	0 min	10 min	20 min	30 min	60 min	90 min	XT pulp	R pulp
Drainability (SR ^o)	24	–	–	–	–	17	17	17
WRV (%)	212	–	–	–	–	195	191	195
Fiber length (mm)	0.976	0.926	0.946	0.937	0.938	0.934	0.939	0.976
Kink index (1/m)	1.300	1.460	1.610	1.620	1.670	1.690	1.690	1.280
Fiber width (μm)	20.8	20.9	20.8	21.0	20.8	20.9	20.9	20.5
Zeta potential (mV)	–81.0 (0.5)	–64.2 (1.4)	–62.2 (0.3)	–63.8 (0.6)	–61.5 (0.1)	–61.3 (0.1)	–60.5 (0.3)	–64.0 (0.4)
WZST strength (Nm/g)	103	–	–	–	–	96	100	107
Bulk (cm ³ /g)	1.62	1.53	1.59	1.54	1.56	1.57	1.50	1.53
Tensile index (Nm/g)	52.7 (2.0)	51.3 (1.4)	48.7 (2.3)	49.9 (2.4)	46.4 (1.6)	46.3 (3.0)	48.4 (1.7)	49.3 (2.8)
Stretch (%)	4.1 (0.3)	3.8 (0.4)	4.1 (0.2)	3.9 (0.3)	3.7 (0.3)	3.5 (0.4)	3.8 (0.3)	3.8 (0.2)
TEA index (J/g)	1.47 (0.17)	1.47 (0.16)	1.48 (0.11)	1.46 (0.18)	1.31 (0.16)	1.23 (0.21)	1.39 (0.13)	1.46 (0.13)
Tensile stiffness index (kNm/g)	6.4 (0.2)	6.3 (0.4)	6.0 (0.3)	6.2 (0.3)	6.0 (0.3)	6.1 (0.3)	6.1 (0.2)	5.8 (0.1)
Tear index (mNm ² /g)	7.6 (0.6)	7.9 (0.3)	7.4 (0.5)	8.2 (0.4)	7.0 (0.3)	8.2 (0.6)	8.0 (0.6)	7.3 (0.1)

treatment of pulps (Kibblewhite and Clark 1996; Oksanen et al. 1997a). Oksanen et al. (1997b) report that removal of 30 wt% of the original amount of pulp xylan with hemicellulase enzymes has no negative effect on the strength properties of non-refined never-dried bleached birch kraft pulp fibers. In this study, it was demonstrated that, with short xylanase treatment times, the effect on the mechanical properties (such as in-plane tensile and out-of-plane tear) of paper is negligible, see Table 2. However, longer xylanase treatment times and the enzyme deactivation procedure seemed to cause some local damage to the fibers in the form of kinks. This observation was facilitated by SEM images; the fibers in sample A (0 min) and R pulp were quite straight and uniform, whereas the fibers in xylanase-treated samples were less straight and damaged fibers were more frequent than in the untreated reference samples. However, there was only a slight reduction in the wet zero-span tensile (WZST) strength due to xylanase treatment. WZST strength gives an indication of the maximum possible tensile strength of the randomly oriented fiber network that can be developed under optimal fiber-to-fiber bonding (Bronkhorst and Bennett 2002). It appears that surface xylan removal from refined never-dried kraft pulp fibers by means of xylanase does not deteriorate the papermaking properties of the pulp and the strength

expectation of the produced paper is at an acceptable level with the xylanase treatment applied in this study.

Conclusions

Endo-1,4-β-xylanase treatment of refined never-dried bleached birch kraft pulp demonstrated selective hydrolysis of xylan from the outermost fiber layers. 2.8 wt% based on the original pulp dry weight was hydrolyzed during the first 10 min of xylanase treatment, indicating a rapid and specific xylan hydrolysis rate. 90 min of treatment removed 3.6 wt% of material (14.2 wt% of the total amount of xylan in the studied pulp) representing mainly the fiber surface xylan, which was confirmed by theoretical evaluation.

The fiber ultrastructure and interfacial properties were detected by SEM and AFM, respectively. The measurements indicated slight microscopic changes in the never-dried fiber ultrastructure, whereas in the nano-scale 3D topography of the fiber and interfacial properties, the differences were more distinguishable. The topographical structure of the fibers further confirmed the surface selective action of xylanase. Interestingly, the concomitant deterioration of the physicochemical properties of the pulp due to xylanase treatment after refining was minor. This enables

the use of xylanase-treated fibers in papermaking or as a platform fiber with high cellulose concentration on the surface layer for further chemical modification.

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