



# FRIEDRICH-SCHILLER- UNIVERSITÄT JENA

## Dissertation

# **Influence of the variability in pulp quality on the alkalization processes**

## **Dissertation**

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Friedrich-Schiller-Universität Jena  
von Diplom-Holzwirtin Catharina Fechter, geb. Kockmann  
geboren am 7. Dezember 1975 in Buxtehude, Deutschland

Gutachter:

1. Prof. Dr. Thomas Heinze, Friedrich-Schiller-Universität Jena

2. Prof. Dr. Fischer, TU Dresden

(3. ....)

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For every complex problem there is an answer that is clear, simple, and wrong.

HL Mencken



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## List of abbreviations

AC	alkali cellulose, based on alkali treated pulp
AGU	anhydroglucose unit
aq.	aqueous
AXU	anhydroxylose unit
Ca	content of amorphous cellulose
CED	copper ethylene-diamine solution
Cell I	cellulose I
Cell II	cellulose II
CI	crystallinity index
CMC	carboxymethyl cellulose
CMX	carboxymethyl xylan
DM	drying machine
DP	degree of polymerization
DP <sub>n</sub>	number-average degree of polymerization
DP <sub>w</sub>	weight-average degree of polymerization
DS	degree of substitution
DT	degree of transformation
DWP	dissolving wood pulp
e or E	elevated content of extractives (e < E)
ECF	elemental chlorine free bleaching
FSP	fiber saturation point
GPC	gel permeation chromatography
-hp	highly pure
HPAEC	high-performance anion-exchange chromatography
HW	hardwood
HWk	hardwood kraft pulp
HWs	hardwood sulfite pulp
k	kraft process
LFAD	lateral fibril aggregate diameter
LFD	lateral fibril diameter
M <sub>n</sub>	number average molecular weight
M <sub>w</sub>	weight average molecular weight
n.d.	not determined

Na-Cell	sodium cellulose
NMR	nuclear magnetic resonance spectroscopy
PAD	pulsed amperometric detection
PDI	polydispersity index
PHK	prehydrolysis kraft process
PP	paper pulp
R	residue
r.h.	relative humidity
R10	residue of the pulp after extraction with 10 wt% aq. NaOH
R18	residue of the pulp after extraction with 18 wt% aq. NaOH
rAC	regenerated alkali cellulose, based on alkali treated pulp
Raman	Raman spectroscopy
RMSE	root mean square error
s	sulfite process
SEC	size exclusion chromatography
SMCA	sodium monochloroacetate
SSA	specific surface area
SW	softwood
SWk	softwood kraft pulp
SWs	softwood sulfite pulp
TCF	totally chlorine free bleaching
WAXS	wide-angle X-ray scattering
WRV	water retention value
wt	weight
VSF	viscose staple fibers
x or X	elevated content of xylan ( $x < X$ )

# 1 Introduction

## 1.1 Background

Pulp originates from the Latin 'pulpa' meaning 'flesh' and is used in many contexts. Within processing technology, 'pulp' means a fibrous substance, forming a slurry when suspended in water. Wood pulp is defined as pulp produced from lignocellulosic plants and consists of liberated lignocellulosic fibers. Wood pulp is a feedstock whose end products are used in diverse markets. Typical consumer goods based on wood pulp are paper, packaging board, absorptive hygiene products, plastic composites, textile fibers and films. Dissolving wood pulp (DWP) is a wood pulp which is purified to a high cellulose content and further processed by dissolution of its molecules, where the fibrous shape is subsequently lost. Its counterpart is PP (paper pulp), which retains its fibrous structure in the final product.

The annual production capacity of dissolving wood pulp (DWP) has increased from less than 3 million tonnes in 2000 to 8 million tonnes in 2019 (Lansdell 2020). Significant growth rates in dissolving pulp production began from 2010 onwards when prices for dissolving pulps reached all-time-high levels of USD1,200 per tonne. 90 % of DWP is processed to viscose staple fibers (VSF), a substitute for cotton. The high price for DWP was driven by increased demand for textile fibers in general and a bad harvest of cotton specifically. Demand for textile fibers increased from 55 million tonnes per year in 2000 to 80 million tonnes per year in 2010 (Lansdell 2020). This increased demand was seen as a long-term trend driven by the increase in world population, prosperity as well as demand for fashion and other related consumer products. Demand for textile fibers is mainly served by oil-based synthetic fibers and cellulose fibers (mainly cotton). The two generic fiber types have entirely different moisture management properties, with cellulose fibers being hydrophilic and able to absorb water. This desired property leads to a cumulative minimum share of cellulose fibers in textiles of ca 35 % (Engelhardt 2013). Since 2005, the production of cotton has stagnated at ca 25 million tonnes per year (Engelhardt 2013, Lansdell 2020, Rex et al. 2019). This so called "peak cotton" was reached because of environmental issues such as extensive land use and drastic use of pesticides. Therefore, the growth in total fiber consumption was forecast to be

covered by man-made fibers, with cellulosic man-made fibers, namely viscose and even new developed types of cellulosic fibers, taking an increasing share. The dominating raw material for the production of man-made cellulosic fibers is DWP. Accordingly, global DWP capacity increased during the last decade by converting paper pulp mills or building greenfield mills bringing new DWP products to the market. Those pulp qualities differ by their wood source, the process and specific equipment used. Along general lines, short fiber sulphate pulps dominate today's available capacities. In 2000, sulfite pulps from both short and long fiber were the most common grades on the market. This change challenges the consumers of DWP, mainly viscose producers, to focus on the relevant quality demands of the new pulps and to be able to fine-tune the process.

Common practice is to control standardized key properties of the dissolving pulp including the average degree of polymerization, determined as intrinsic viscosity, hemicellulose content, resistance to alkaline extraction, determined as R18- and R10-value (with 18 and 10 wt% aq. NaOH at 20 °C, respectively) and content of extractives and inorganics. As it is common practice to mix several pulp qualities in the production of one viscose fiber product, it is difficult to track back occurring production problems to specific pulp qualities.

## **1.2 Objectives and thesis outline**

Increased dissolving pulp capacity from new dissolving pulp products entering the market means there is a need to describe the available quality span, and reflect upon the functionality in industrial processes and the magnitude of deviations leading to problems in processability.

This work characterizes first a broad variety of recent market dissolving pulps by means of typical specified properties, other standard properties and in-depth analysis of structural properties (4.1). No literature is available to date which provides such a comprehensive overview of the properties of generic pulps including a quantification of the variety within one product group. From those pulps, a few were selected for a comprehensive description of their behavior in specific alkaline treatments by means of alkaline extraction (4.2). The behavior of dissolving wood pulp (DWP) in alkaline medium is of special interest as the

commercially most important applications of DWP, viscose fibers and carboxymethylated cellulose, start with an alkaline activation of the pulps. The presented studies investigated the effect of the chosen alkalization technique and how the initial intrinsic viscosity of one model pulp influences the result of the alkalization (4.2.1 and 4.2.2). The contradicting parameters process yield and purity were investigated in detail for three selected pulps by studying a wide span of different alkalization settings (4.2.3). A smaller and more realistic span of settings was then applied on one of the pulps and a model for the alkalization yield at typical full-scale conditions proposed (4.2.4 and 4.2.5). Pulp yield after alkalization is important for two reasons. It determines the composition and processibility of the resulting press lye, and it is one parameter for the total process yield of the end product. Consequently, even the effect on non-saccharides present in the pulp and the composition of the resulting press lye for representative generic pulps are presented in 4.2.6 and 4.2.7.

Market dissolving pulps are traded globally and always finished by drying. Structural changes induced by drying are often seen as a probable explanation for deviations in processability. 4.3 addresses this issue by investigating the possible span of structural properties due to different drying procedures.

Finally, one common application of DWP was investigated towards the product properties in relation to the used pulps (4.4). Here, the procedure of carboxymethylation of alkalized pulp was chosen as it was not possible to simulate the more common viscose process at lab scale during the project preceding this thesis.

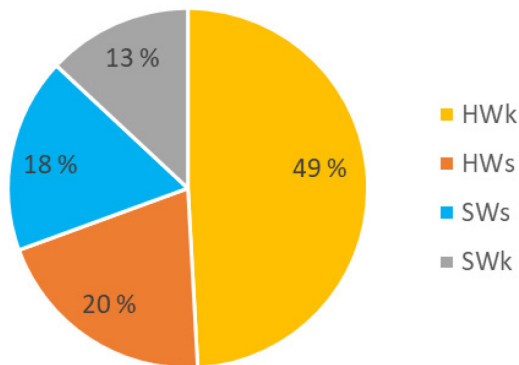
The hypothesis of the study is that the variation within one group of generic dissolving pulps is higher than the variation between the different generic dissolving pulps. If this is the case, it becomes important to consider the optimization of further processing.

## 2 Literature review

### 2.1 The variety of dissolving pulps

#### 2.1.1 Generic dissolving wood pulp

Dissolving wood pulps (DWP) are derived from either softwood (SW) from coniferous trees or hardwood (HW) from deciduous trees. SW yields long-fiber pulp with a mean fiber length of  $> 1.5$  mm; HW yields short-fiber pulp with a mean fiber length of  $< 1.5$  mm. Two process concepts with the target to liberate the cellulosic fibers by eliminating the lignin matrix are established and well described in literature (Sixta 2006b, Fengel and Wegener 1989). The alkaline kraft process uses NaOH and Na<sub>2</sub>S and the acid sulfite process uses SO<sub>2</sub> in combination with a base (usually Mg<sup>2+</sup>) as active chemicals. More than 60 % of global DWP capacity is produced using the kraft process, and almost 70 % of global DWP capacity uses hardwood as raw material (Pöyry 2020, Figure 1).



The optimal wood cooking process for production of DWP decomposes and solubilizes the lignin and hemicelluloses, while it preserves the cellulose at the same time. In the sulfite process, hemicellulose reduction is rendered possible during the cooking at moderate yield loss of cellulose. As this is not possible for the kraft process, additional treatment steps are used, such as acid prehydrolysis prior to cooking or alkaline extraction steps after cooking with temperatures far below the cooking temperature of ca 150 °C. Cooking loosens



the tight structure of the wood fiber composite and defines the accessibility of the remaining fiber structure with pores left after the dissolved compounds. Pulps cooked according to the sulfite and the kraft process are then bleached with several bleaching steps at shifting pH alternating with washing steps. The alkaline conditions in the kraft process require chlorine-containing bleaching chemicals to reach sufficient purification of the pulp. 70 % of existing kraft pulp mills producing DWP bleach with modern elemental chlorine-free sequences (ECF) where  $\text{ClO}_2$  is used. The remaining mills use the more hazardous elementary chlorine or  $\text{ClO}^-$  in their bleaching sequences (Pöyry 2020). More than 40 % of sulfite mills bleach with totally chlorine-free sequences (TCF) using chemicals such as  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$ ,  $\text{O}_2$  or  $\text{O}_3$  and  $\text{CH}_3\text{-CO}_2\text{OH}$  as the pulp is more easy to bleach due to the acid cooking mechanisms.

### **2.1.2 Characterization of dissolving pulps**

Primarily, dissolving pulps are classified by their purity in terms of cellulose content and the molecular weight of the cellulose. Parameters commonly used to describe these properties are the R18-value and the intrinsic viscosity.

The intrinsic viscosity is an indirect measure for the mean molecular weight of the pulp. Depending on the application area, i.e. quality of the viscose or type of derivative, pulps are grouped in low- and high-viscosity pulps and low- and high-alpha pulps. High-viscosity and high-alpha pulps reach higher market prices than standard qualities used for standard viscose staple fibers (VSF).

The R18-value correlates to the content of high molecular weight cellulose in the pulp and is the residue of the pulp after extraction with 18 wt% aq.  $\text{NaOH}$  at 20 °C and subsequent washing with acetic acid. It is still common to describe a pulp by its "alpha-content". Here, one refers fundamentally to the Tappi method T203 "Alpha-, Beta- and Gamma-Cellulose in Pulp", the standard set by the Technical Association of the Pulp and Paper Industry. Even though this standard is still active with its recent version T203 cm-09 from 2009, it is not widely used for the practical quality control of DWP, as the procedure comprises unpredictable human factors when displacing the high concentrated lye in the residue by lower concentrated lye. The washing procedure using diluted lye makes the lye concentration in the pulp passing its solubility

maximum of ca. 10 wt% aq. NaOH. This is the reason for the alpha-content being lower than the R18. Götze (1967) noted already that the alpha-method has been replaced by the R18-value since the 1940s. Today, communicated alpha-contents are usually calculated from the R18 and the residue of the pulp after extraction with 10 wt% aq. NaOH (R10) as

$$\text{alpha} - \text{cellulose} = \frac{R18-R10}{2} [\%] \quad \text{Equation 1}$$

Other important properties connected to the purity of the pulp are the content of other carbohydrates like xylan and mannan, extractives and mineral content. Extractives are determined using acetone, DCM or ethanol. A detailed characterization of the compounds in the extracted substance is not standard. Minerals in the pulps are analyzed as ash or specific metal content. The metal content might be expressed as its ion or as oxidized equivalent. Metals in focus are Ca, Mg and Si as they are supposed to precipitate on the equipment or in the fiber pores and by this hinder the availability of the cellulose (Götze 1967). Fe and Mn are of special interest as they positively catalyze the oxidative degradation of carbohydrates in alkaline medium and have to be controlled (Samuelson 1967). The commercially used catalyst Co is of lower interest as it does not commonly occur in detectable amounts in pulp. Cu has to be monitored as it negatively catalyzes the oxidative degradation of carbohydrates in alkaline medium (Götze 1967).

### **2.1.3 Basic differences between generic dissolving wood pulps**

Dissolving wood pulps from hardwood or softwood, produced according to the kraft or sulfite process, are most obviously characterized by different fiber morphology (long and short fibers). Chemical composition and the ultrastructure of the fibers differ, too (Duan et al. 2015, Fengel and Wegener 1989, Li et al. 2018, Sixta 2006a and 2006b). Table 1 summarizes important differences between sulfite and kraft dissolving pulps and the process and raw-material related reasons for these differences as described in literature.

**Table 1: Process and raw material related differences between generic wood pulps as described in literature (Duan et al. 2015, Engstrom et al. 2006, Fengel and Wegener 1989, Fischer and Schmidt 2008, Gehmayr and Sixta 2012, Götze 1967, Hamilton and Thompson 1960, Jayme and Koeppen 1950, Luce 1964, Page 1983, Sixta 2000, Sixta 2006b, Young 1994)**

	<i>Kraft pulp</i>	<i>Acid sulfite pulp</i>
Mechanism of delignification	Degradation of lignin to lower DP and dissolution in alkaline medium	Sulfonation of lignin and dissolution in aqueous medium
Mechanism of carbohydrate degradation	Swelling in alkaline medium and peeling-reactions at the reducing end-group	Randomly cleavage by acid hydrolysis
Cell wall degradation	Less extensive	Extensive
Fiber morphology	More narrow fiber length distribution and less fines	Wide fiber length distribution and more fines
Degree of polymerization	Even distribution over the cell wall Narrow distribution of molecular weight Lower intrinsic viscosity	Gradient from the lumen to the fiber surface Broader molecular weight distribution with high content of low molecular weight fraction Higher intrinsic viscosity
Pores in pulped fiber wall	Smaller pores and smaller pore volume	Large pores and high pore volume
Carbohydrate composition		
- Mannan	Mannan is mainly removed	Some mannan remains in the fiber cell wall equally distributed
- Xylan	Parts of the xylan remain precipitated on the fiber surface	Xylan is mainly removed
- R18 <sup>a</sup>	>95 %	>92 %
Extractives	Resin and fatty acids can be saponified and removed. Neutrals are more difficult to approach.	Most suitable for wood species with low content of resin acids as phenolic compounds condensate with lignin and impede delignification.

<sup>a</sup> R18 – residue after alkaline extraction with 18 wt% aq. NaOH

The acid conditions in the sulfite process yield a heterogeneous fiber, both in terms of fiber morphology and molecular weight as the degrading reactions proceed from the primary wall to the secondary wall layers by random acid hydrolysis of the carbohydrates (Jayme and von Koeppen 1950, Page 1983). The primary wall is largely destroyed in the ready pulp (Fischer and Schmidt 2008, Young 1994). The alkaline conditions in the kraft process swell the fiber structure and impregnate the fiber with active chemicals. The reactions take place uniformly over the fiber cross section (Page 1983) and the degree of polymerization is more uniform across the fiber cross section compared to sulfite pulps (Jayme and Van Koeppen 1950, Luce 1964). Parts of the primary cell wall might endure in the kraft process in those cases where milder conditions are applied (Fischer and Schmidt 2008, Young 1994). The fact that much research has shown that sulfite pulps have larger pore volume and pore size than kraft pulps (Duan et al. 2015, Engstrom et al. 2006, Gehmayr and Sixta 2012) can be attributed to the randomly proceeding acid hydrolysis in the sulfite pulps and the peeling-reactions in the uniformly swollen structure of the kraft pulps.

The above-mentioned differences between the kraft and the sulfite process lead to differences in the degradation of the carbohydrates. The branched xylan is known to be well degraded and removed under the acid conditions of the sulfite process while the alkaline conditions in the kraft process attack the xylan to a lesser extent (Hamilton and Thompson 1960, Sixta 2000). Kraft pulps potentially possess a higher xylan content due to the alkaline conditions of the process. This tendency is even more distinct for pulps made from hardwood owing to the high initial xylan content in that wood (Sixta 2006b). Linear mannan as well as degraded cellulose are more easily removed from the swollen cell wall structure occurring in the kraft process than from the randomly perforated cell wall occurring in the sulfite process.

Both the sulfite and the kraft process might be adapted to match different target compositions. In the case of the kraft process these adaptations are made by adding pre- or posttreatments. Most commonly implemented is the acid prehydrolysis (PHK). Posttreatments with hot or cold alkali are implemented

for “high-alpha”-pulp reaching cellulose >97 %. The sulfite process is commonly adapted directly in the cooking process by tuning the parameters.

The extractives content also affects the purity of dissolving pulp. Common understanding is that extractives impair the viscose process by clogging equipment and discoloring both the viscose solution and the fiber product. The extractives in wood can be categorized into acid and neutral organic compounds. The main groups within the acid compounds are fatty acids and resin acids. Under the alkaline conditions of the kraft process, the acid compounds are saponified and, to a large extent, dissolved in the cooking and washing liquors. Neutrals are more difficult to approach in the cooking step, but they can be dispersed in the saponified acids and washed out after cooking. Under the acidic conditions of the sulfite process, even the acid compounds are affected only mildly and, thus, remain in the pulp. Efficient washing after the cooking stages is then less helpful in removing extractives from the sulfite process compared with the kraft process (Hillis 1962, Fengel and Wegener 1989). Certain extractives, such as the neutral component pinosylvin (a stilbene in pine heartwood), are involved in condensation reactions together with lignin and lead to worse processability in the pulping line. Accordingly, pine species containing pinosylvin are avoided in acid sulfite pulping. Dispersion of neutrals with surfactants, including the soaps of the acid wood extractives formed in the kraft process, makes a reduction in the pulp washing line possible, but will not lead to complete elimination. As the extractives in HW-pulps are generally of more neutral nature they are supposed to have a more negative influence on the viscose process (Götze 1967). Dispersed residual saponified resin acids in the dissolving pulp might in turn have a positive effect on the viscose process (Götze 1967). As early as the 1960s, surfactants were actively added in the viscose process in order to improve both the alkalization and the xanthation reactions in the viscose process based on this principle of improved dispersion (Götze 1967).

Owing to long-term practical experience, producers of cellulose derivatives or cellulose fibers have distinct preconceptions of pulp types. It is commonly assumed that sulfite pulps have a higher accessibility and thus reactivity on the positions 2, 3 and 6 (Duan 2015, Fengel and Wegener 1989, Götze 1967, Sixta

2000) than kraft pulps. The pulp purity and the supramolecular structure of the polymers are expected to play a key role in forming these differences between pulps. Remaining parts of the primary wall and smaller pore size and volume are possible reasons for the lower ranked reactivity of kraft pulps (Duan et al. 2015). Anyhow, sulfite pulps might cause reactivity issues due to the higher share of low molecular weight material. This low molecular weight material reacts rapidly with NaOH or the derivatizing agent and causes incomplete reaction on the high molecular weight substance (Sixta 2006b). In the ready spun cellulose fiber, low molecular weight substance causes lower fiber strength, especially wet strength, and makes the pulp unsuitable for high-tenacity demands (Treiber 1983).

## **2.2 The supramolecular structure of pulps**

Many different models for describing the structure of the lignocellulosic cell wall and the hierarchy of its components have been proposed (Hearle 1958, Fengel 1970, Scallan 1974, Ding and Himmel 2006). The scope of this work is not to highlight or disapprove specific ones, but to take their consensus as the most probable assumption for the construction of the cell wall. They have in common that they describe cellulose as a heterogeneously structured polymer consisting of a mixture of low-ordered amorphous regions and highly-ordered crystalline regions. The amount of crystalline parts in this semi-crystalline structure, indicated by the crystallinity index (CI), depends on the origin and processing of the cellulose. Typical values for the CI of wood pulps determined with X-ray diffraction are 50 to 60 % (Sixta 2006b). Moreover, the cell wall is described as having different hierarchical ordered elementary structures of arranged cellulose chains surrounded by hemicellulose and lignin. Cellulose and specifically its crystalline regions are generally considered to build up the backbone of the structure. Starting from the smallest level of cellulose structure these hierarchical levels are denoted as cellulose chain, elementary fibril (closely, parallelly aligned cellulose chains (Fengel 1970)), fibril aggregate and microfibril. The higher hierarchical levels comprise all three components and are denoted as microfibril, macrofibril or fibril which build up the lignocellulosic fiber. Here both crystalline and amorphous cellulose are

included. The size of some of the structural elements can be estimated by different indirect methods where the chosen cell wall model sets the logic for the evaluation. The dimensions of the single crystallites in a microfibril determined with X-ray diffraction are given as 4.5 – 5 nm in width and 5.5 – 6.7 nm in length (Sixta 2006b). The macrofibrils or fibril aggregates are described to be 10-30 nm in diameter and a few hundred nanometer long (Pönni et al. 2012). Cooking, bleaching and washing of wood raw material affects the structural properties of the resulting pulp when removing the middle lamella, the primary and parts of the secondary wall and consequently changes the chemical composition of the material towards more cellulose. This event is known to loosen up the fiber wall and to create pores. Evans et al (1995) have shown the crystallinity to increase at the same time as less ordered components of the material have been removed. The upcoming reticular pore system is seen to consist out of micro- and macropores. The intrafibrillar micropores are estimated to a size of a few nanometers, and the interfibrillar macropores are estimated to a size of up to 50 nm (Stone and Scallan 1967, Maloney and Paulapuro 1999, Grönqvist et al. 2014).

It is well documented that porosity decreases upon drying. Östlund et al. (2010) have shown small pores (2 - 10 nm) to be affected mostly when exposed to drying and that more severe drying conditions (oven drying instead of air drying) even affects larger pores. This change in supramolecular structure is referred to as hornification and was firstly quantified by the irreversible decrease of the water retention value WRV (Jayme 1944, Laivins and Scallan 1993). The mechanism is seen to be cross-linking between cellulose microfibrils due to hydrogen bonds when the supramolecular structure collapses upon water removal from the fiber wall. Even co-crystallisation of adjacent microfibrils, which are parallel over a sufficient distance, has been proven to occur (Newman 2004). It has even been known for long time that hemicelluloses hinder hornification by acting as spacer between cellulose fibrils (Spiegelberg 1966, Köhnke et al. 2010, Khanjani et al. 2017). It is important to understand the mechanism of hornification in dissolving pulps as hornified fibers have a tendency to contribute to lower reactivity towards reactants and by this to undissolved fibers when aimed for dissolving (Götze 1967).

## 2.2.1 Measurement of the supramolecular structure of pulps

### 2.2.1.1 Spectroscopic methods

Most common practice is to characterize the supramolecular structure of the cellulose lattice in the loosened fiber wall by exposing the sample to electromagnetic waves. X-ray scattering (XRD), solid-state  $^{13}\text{C}$ -NMR spectroscopy (NMR) and Raman spectroscopy (Raman) are methods frequently used to determine the degree of crystallization (CI). Even algorithms for the determination of the portion of cellulose II and the crystallite size have been developed (3.2.5). The methods deliver precise results with high reproducibility. Anyhow, the interpretation of the results is complex as many different signals compile the specific information of one measurement. No standards to determine structural parameters have been decided yet. Even for one method, several approaches for the evaluation of one property are proposed in literature (Park et al. 2010). The heterogeneous and imperfect crystalline structure of the cell wall makes it impossible to use different indirect measurement techniques and analysis methods to determine one strictly defined property. Each method is sensitive to different aspects of the order and disorder of the heterogeneous material and the outcome from the measurements should rather be taken as a structure related classification figure from each technique and method applied.

XRD, more specifically WAXS (wide-angle x-ray scattering), measures the proportion of molecules within regions of long-range order. The isotropic nature of pulp samples implies a challenge to gain sufficient measurement resolution and the variety of diffraction peaks proposes different approaches for data analysis. Thygesen et al. (2005) have applied four different established methods for the analysis of XRD-data and have found a CI for one sample of purified cellulose material to be 39 – 67 %.

Solid-state  $^{13}\text{C}$ -NMR spectroscopy is as the method version CP/MAS  $^{13}\text{C}$ -NMR (dipole-dipole  $^1\text{H}$  decoupled cross polarization magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy) widely used to determine structural properties of semi-crystalline organic solids, e.g. cellulosic material. The spectra consists of four signals especially emerging the C-atoms within the glucose molecule (C-1, C-4, C-2,3,5 and C-6). The signals can be deconvoluted and



approaches for data analysis regarding the determination of cellulose allomorphs and crystallite sizes are proposed in literature (Atalla and VanderHart 1984, Larsson et al. 1997, Newman 1998, Wickholm et al. 1998, Atalla and VanderHart 1999, Hult et al. 2000, Newman 2004, Olsson et al. 2014). The C-4 signal (chemical shift 80-90 ppm) is particularly well separated and contains information on cellulose I allomorphs, cellulose II, portions of inaccessible cellulose within the interior of crystallites and accessible surfaces.

Raman spectroscopy is based on the Raman-effect that molecules scatter parts of the irradiated electromagnetic waves inelastically. Interest in Raman-spectroscopy within wood science has increased since the beginning of the 20<sup>th</sup> century (Agarwal and Ralph 1997, Schenzel and Fischer 2001, Schenzel et al. 2005, Agarwal et al. 2010). The changed frequency and wavelength of the scattered residual electromagnetic waves of the IR-light source detect indirectly the oscillation of the macromolecular lattice. The spectrum is hence used for the empirical determination of the supra-molecular structure of the lignocellulosic cell wall.

#### 2.2.1.2 Methods based on adsorption phenomena

Methods aimed at determining pore size, pore size distribution and the resulting accessible surface and volume are commonly based on adsorption phenomena when saturating the fiber wall with suitable substances, e.g. water (fiber saturation point FSP, water retention value WRV, cryoporometry), mercury (mercury-intrusion porosimetry) or nitrogen (Brunauer-Emmett-Teller BET). Regarding the above discussed issue of hornification (2.2), methods operating in wet or re-wetted states are those which deliver relevant results.

The determination of the water retention value (WRV) uses an unlaborious measurement technique reflecting different properties in a pulp sample. The specific outer surface area of the particles, the hydrophilicity of the different chemical components (hemicellulose associates strongly with water) and the pore volume are mirrored when measuring the amount of water left in the sample after centrifugation. The centrifugation removes the water between fibers and inside the lumen of the fibers; in consequence, the remaining water

is localized mainly in the pores of the fiber wall giving a measure for the pore volume.

Another well-established method, which measures solely the amount of water within the cell wall and accordingly the pore volume of the cell wall, is the determination of the fiber saturation point (FSP). Instead of measuring the remaining mass of water left in the sample after forcing the surplus of water from the structure, this method measures the dilution of a polymer of well-defined size dissolved in water added to the water-saturated sample. This method is more complex compared to the determination of WRV.

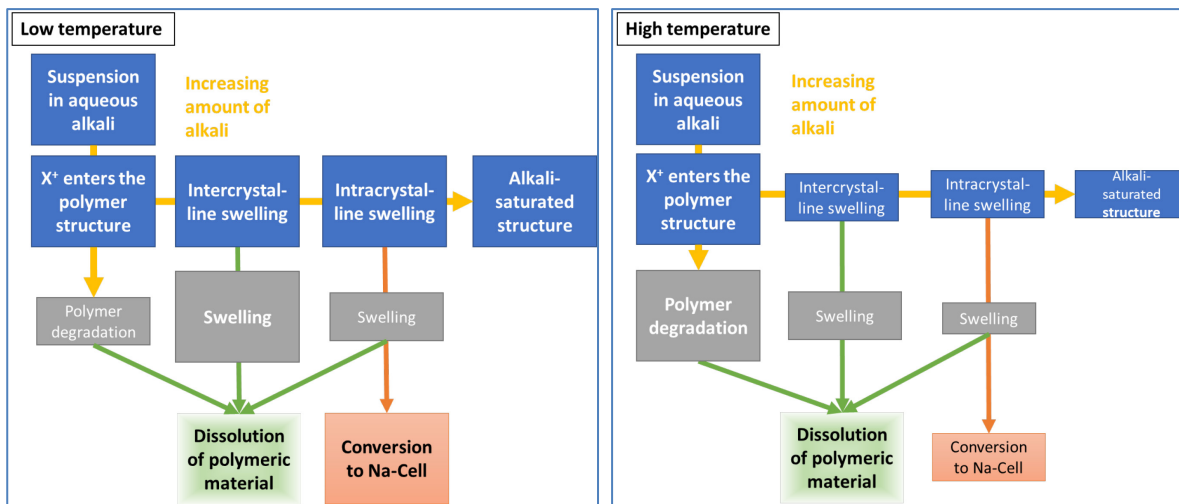
### **2.3 Alkali treatment of dissolving pulps**

Nearly 90 % of global DWP is processed in alkaline medium. These alkaline based processes are the viscose process for production of man-made fibers, using more than 75 % of DWP-volume, and processes turning the cellulose into cellulose ethers with carboxymethyl cellulose (CMC) being the most important product (Lansdell 2020).

Alkalization of the pulp is the first of four main steps when producing viscose fibers (Götze 1967). The other three are xanthation, dissolution in alkaline medium, and extrusion and precipitation of viscose fibers into acid medium. The alkalization yields swelling of the cellulose and improves the nucleophilicity of the hydroxyl groups by forming sodium cellulose (Na-Cell). Specifically, in the established viscose process, the pulp/alkali-slurry is pressed of to a water content of ca 50 wt% yielding alkali cellulose (AC) consisting mainly out of Na-Cell. Na-Cell is able to react in the following process steps. The preaging, as part of the alkalization step, aims for a controlled oxidative depolymerization of the Na-Cell. The reaction kinetics for specific pulps and its initial intrinsic viscosity are used to be modelled with an empirical approach in dependence of the reaction time and temperature (Eklund 2021). The preaged AC containing Na-Cell with an adapted degree of polymerization (DP) is able to react with carbon disulfide in the subsequent xanthation step. Pulp, evenly substituted with xanthate groups, will be soluble in alkaline medium. Substitution of every fifth or sixth hydroxyl group – corresponding to a degree of substitution (DS) of 0.5 - will be sufficient to yield a viscose solution free of

pulp fibers (Götze 1967). Insufficient dissolution of only 0.1 % of the pulp fibers will make the solution unprocessable as the dissolved pulp cannot be spun, i.e. extruded, and regenerated to strong man-made fibers of adequate fineness. The solution will not even pass the filters with a pore size of about 60 - 10  $\mu\text{m}$  prior to fiber spinning. The solubility of the pulp is the key property when shaping man-made cellulosic fibers, and the initial alkalization is the precondition for an effectual xanthation which then controls the solubility. Activation with alkali must be adjusted to the pulp used (Sixta 2006b). Various types of pulp are on the market that may differ in purity, ultrastructure, and various other parameters and, consequently, in reactivity. The term reactivity is of importance because it describes the applicability of the pulp to be converted within a specific chemical process – here alkalization.

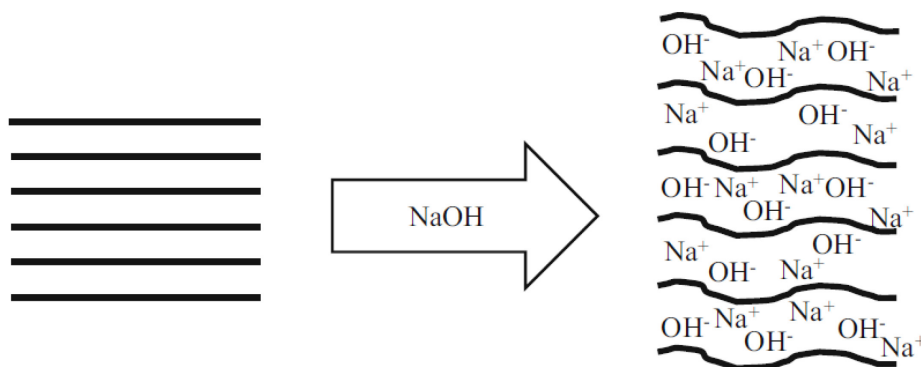
Changes in the pulp induced through alkalization have been intensively considered in research and have been established and well described by Rydholm (1965), Fengel and Wegener (1989), Woodings (2001) and Sixta (2006a). When treating pulp with aqueous alkali, the composition, and the polymer structure in terms of configuration and size distribution are changed depending on the temperature and alkali concentration applied. Swelling of the entire solid polymer structure in alkali will lead to both transforming the cellulose part into Na-Cell, and the dissolution of polymers with a low DP, i.e. hemicelluloses and low-molecular fractions of the cellulose. How these changes are connected to each other is illustrated in Figure 2 and described below in more detail.



**Figure 2: Schematics for alkali treatment of cellulosic material at increasing alkali concentration. The size of the rectangles implies the extent of the phenomenon. Left: Treatment at low temperature. Right: Treatment at high temperature.**

### 2.3.1 Sodium cellulose

The amorphous regions of a pulp are easily accessible when dispersed and swell in any polar solvent. Adding NaOH to H<sub>2</sub>O will immediately swell even less accessible regions and turn the cellulose molecules into sodium cellulose (Na-Cell) as illustrated in Figure 3 (Heinze et al. 2018). This structure will exceed the degree of swelling compared to dispersion in pure water as even higher amounts of the solvent are incorporated in the structure due to the more polar character of the Na-Cell (= Cell-O<sup>-</sup>---H<sup>-</sup>---OH<sup>-</sup> Na<sup>+</sup>) compared to cellulose.



**Figure 3: Schematic illustration of the transformation of a cellulose crystallite into activated sodium cellulose by aqueous NaOH (Heinze et al. 2018)**

The crystalline regions, which account for ca 50 % of the pulp, will not swell at the same conditions. Given the fact that interactions with cellulose take place at the hydroxyl groups at Position 2, 3 and 6, it is implicated that a high CI and large crystallites will decrease the reactivity towards sodium ions as the amount of available hydroxyl groups becomes considerably lower. Anyhow, the crystalline regions will swell and become accessible depending on the conditions applied. A distinction is drawn between easily achieved intercrystalline swelling, i.e. filling the pores between the crystallites, and intracrystalline swelling. Whether intracrystalline swelling occurs or not, depends on the alkali concentration and temperature of the suspension. At room temperature, intercrystalline swelling passes into intracrystalline swelling at an alkali concentration of around 9 wt% aq. NaOH. Intracrystalline swelling is completed at about 15 wt% (Rydholm 1965). Heuser and Bartunek (1925) and Saito (1939) have found a maximum total swelling of rayon at around 9 wt% (Figure 4). Richter and Glidden (1940) identified 10-12 wt% as the maximum for different wooden pulps and cotton linters. Total swelling levels off upon a further increase in alkali concentration when intracrystalline swelling takes place and intercrystalline swelling decreases. This is a result of competing reactions between cellulose, H<sub>2</sub>O and the Na<sup>+</sup>OH<sup>-</sup> dipole when reactants penetrate the cellulose structure (Klemm et al. 1998; Sixta 2006a). As swelling of cellulose is an exothermic process, increasing the temperature decreases the total swelling and increases the aqueous alkali concentration needed for obtaining a specific state of swelling (Saito 1939).

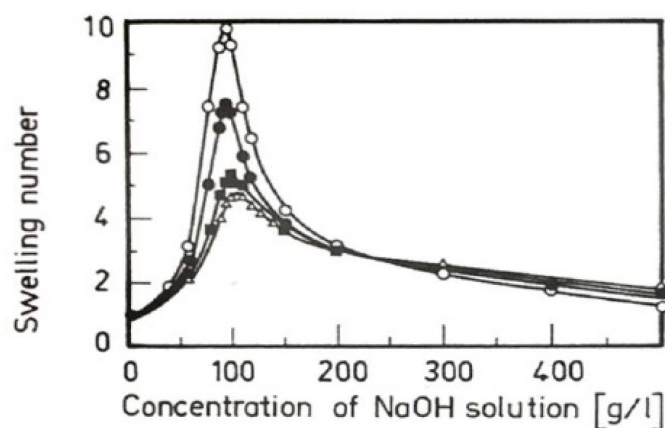


Figure 4: Swelling number of rayon in aqueous NaOH at ◦14, •20, ▪25 and Δ31 C (Saito 1939)

However, intracrystalline swelling of the structure in a highly alkaline medium converts crystalline cellulose into Na-Cell and breaks hydrogen bonds in the cellulose structure. This process makes the hydroxyl groups located in the crystalline regions of the cellulose accessible for subsequent chemical reactions. A full lattice conversion to Na-Cell in alkaline medium will activate the whole structure and makes it available for further reactions.

Native cellulose exists as the specific lattice cellulose I (Cell I). When washing and neutralizing Na-Cell, and thus removing NaOH, regeneration into the thermodynamically more stable crystal lattice of cellulose II (Cell II) takes place. An analysis of the change in content of Cell II before and after alkalization and regeneration gives information on the resistance of a specific pulp to alkalization. Accordingly, it is possible to follow the performance of the alkalization by mapping the degree of transformation from cellulose I (Cell I) to cellulose II (Cell II) after the alkalized pulp has been neutralized and washed (regenerated) (Reyes et al. 2016). Nevertheless, Fink et al. (1982) has discovered that the regeneration of partially alkalized pulp does not lead to the complete transition from Na-Cell to Cell II, as parts of the Na-Cell have been supposed to regenerate back to Cell I (Figure 5). It has been shown that this behavior is less pronounced in relative terms when more Na-Cell is built. Rydholm (1965) has indicated an incomplete transformation of Na-Cell to Cell II upon regeneration as well and the explanation given has been the increase in amorphous cellulose.

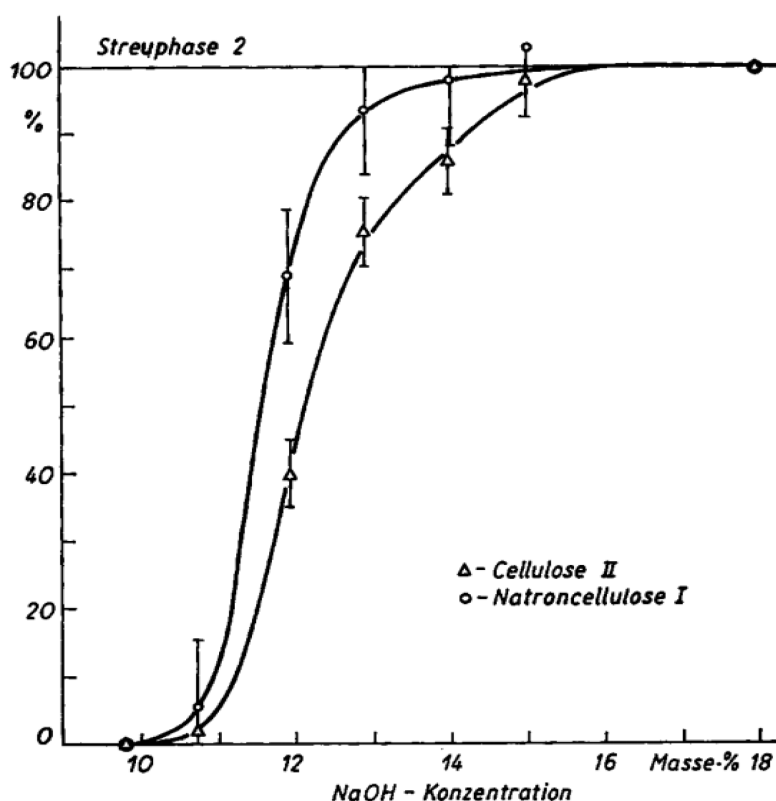
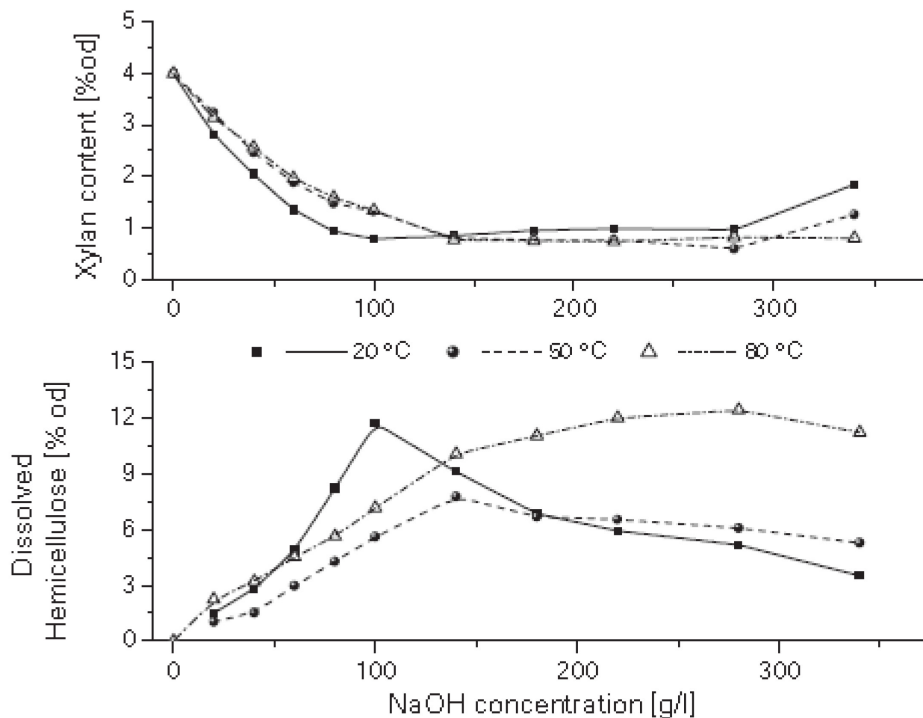


Figure 5: Proportion of Na-Cell and Cell II depending on the concentration of NaOH after alkalization and subsequent regeneration of pulp (Fink et al. 1982)

### 2.3.2 Solubility of polymers in alkaline medium

Swelling upon alkali treatment favors the dissolution of polymers, i.e. hemicelluloses and short-chained cellulose, in the pulp. On one hand, exceeding the maximum of total swelling of the pulp by increased alkali concentration or temperature will decrease the amount of dissolvable carbohydrates as the mass transport will be sterically limited. On the other hand, chemical degradation reactions have been shown to appear at temperature levels  $\geq 40$  °C in combination with high alkali concentration of around 18 wt% aq. NaOH (Mozdyniewicz et al. 2014; Sixta et al. 2004). Degradation will create additional alkali-soluble substance. Substance dissolved in the alkali treatment can be removed easily by pressing as it is practiced in the viscose process. Pressed and fluffed Na-Cell is easy to depolymerize by means of the oxidation. This oxidation is done in the aging step prior to xanthation, which is done in order to adjust the degree of polymerization (DP) to the requirements of the viscose

fiber product aimed for. Accordingly, a side effect of pressing the slurry of pulp and aqueous alkali is purification of the pulp dedicated for xanthation by means of alkali extraction. This process ensures, on one hand, the purification from short-chained, xanthation-chemical-consuming polymers. On the other hand, purification causes a yield loss for the viscose mill, which finally depends on the recovery strategy of the press lye. Studying beech sulfite dissolving pulp Sixta and Schrittwieser (2004) have shown that xylan removal has been more efficient at 20 °C than at higher temperatures, see Figure 6. To obtain the lowest possible xylan content in the pulp residue (about 0.7% has appeared to be alkali-resistant) even at raised temperature (50 °C), the NaOH concentration must be increased from 10 % to about 14 %. Moreover, increasing temperatures will cause chemical fragmentation reactions (Sixta et al. 2004) and create different amounts of additional alkali soluble substance depending on the specific pulp. This will both contribute to a lower process yield and increased purity of the pulp to xanthation within the viscose process.



**Figure 6: Profiles of xylan content in the pulp residue (upper) and the of dissolved hemicelluloses (sum of beta- and gamma-cellulose) (lower) during the alkaline treatment of beech sulfite dissolving pulp (93.4 % R18, 4.0% xylan) at different temperatures. Caustic treatment: 5% consistency, 30 min reaction time, NaOH concentrations: 20, 40, 60, 80, 100, 140, 180, 180, and 340 g/l. (Sixta and Schrittwieser 2004)**



### 2.3.3 Industrial conditions for alkalization used in the viscose process

Regarding the viscose process, the optimal choice of steeping conditions, namely alkali concentration and temperature, is a balance between swelling, the extent of transformation to Na-Cell, dissolution of short-chained polymers, which are removed with the lye by means of alkaline extraction through pressing, and the processability of both the press lye and the Na-Cell. An early study (Wyatt 1966) has used an unspecified pulp when optimizing alkalization towards viscose quality and recommends steeping with 18.3 wt% aq. NaOH at 15°C under 27 min as universally optimal process settings. A recent study (Reyes et al. 2016) has worked with a softwood sulfite dissolving pulp for viscose production by modelling the relation of alkali concentration, temperature and time towards yield and transformation to Na-Cell, i.e. the increase in Cell II. They have found the optimum for lattice transformation and yield to be 21 wt% aq. NaOH at 29°C under 45 seconds. The short treatment time reflects the small influence of time during the alkalization of pulp as swelling occurs instantaneously (Rydholm 1965). The optimum has been at 45-50 °C if only the yield is considered.

Today, industrial steeping is commonly done in a slurry with 17-19 wt% aq. NaOH at 45-55°C (Woodings 2001). Previous research studies have mostly referred to sheet steeping (Ellefsen 1955; Kolboe 1960; Kyrklund 1963; Sihtola and Nizovsky 1963), but even the application of today's slurry alkalization has occurred in the past (Treiber 1962). These studies have shown a clear tendency to refer to lower temperatures (20-35°C) fitting to the reported results of the optimization studies named above. A lower lye temperature is known to hamper processability by more viscous lye and more swollen Na-Cell. No former study has reported on influences of pulp characteristics when optimizing steeping conditions in the viscose process.

New pulp qualities have entered the market in the past decade to meet the growing demand for greater viscose production capacity. The difference in pulp qualities available results from the wood source used and the process and equipment applied. These factors challenge the viscose producer to focus on the relevant quality demands of new-coming pulps and to tune the process. Common practice is to control standardized key properties of the dissolving

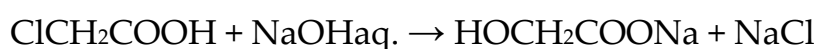
pulp, such as the average degree of polymerization, which is determined as intrinsic viscosity; hemicellulose content; resistance to alkaline extraction, which is determined as R18 and R10 at 20 °C; and the content of extractives and inorganics. It is difficult to track occurring production problems back to specific pulp qualities as it is common practice to mix several pulp qualities in the production of one viscose fiber product.

#### **2.4 The conversion of sodium cellulose into carboxymethyl cellulose**

Etherification is an important branch of the commercial derivatization of cellulose. Cellulose ethers (alkyl, hydroxyalkyl, and mixed ethers) have a broad variety of applications (Dönges 1999; Heinze and Liebert 2012). Ionic carboxymethyl cellulose (CMC) is the most important one regarding industrial produced quantities (Heinze and Koschella 2005).

The raw material when producing CMC is commonly pulp derived from wood or cotton linters. Depending on intended application, these vary in cellulose purity (technical grades might even be produced from paper pulp grades), and intrinsic viscosity, where cotton linters pulp delivers the highest potential.

The process of carboxymethylation is the conversion of the hydroxyl groups of cellulose with monochloroacetic acid or its sodium salt after activation of the biopolymer with aqueous NaOH. Carboxymethylation involves the following competitive reactions occurring simultaneously (Mark et al. 1965):



Prior to etherification, the cellulose must be activated with a treatment using aqueous NaOH. The complete transformation of the cellulose into sodium cellulose (Na-Cell) is a precondition for etherification and for obtaining the desired properties of carboxymethyl cellulose (CMC), such as solubility in water at a degree of substitution (DS) as low as about 0.5 (Heinze and Liebert 2012).

The quality of CMC is commonly described by the degree of polymerization (DP), the degree of substitution (DS), the distribution pattern of substituents, the content of insoluble matter, and the content of the byproducts NaCl and

glycolic acid. The DP of CMC depends on the molar mass of the pulp. The higher the intrinsic viscosity of the pulp, the higher the DP of the CMC. The DP sets the limits for the thickening behavior of the product. The DS and distribution pattern of substituents are set by the process settings and the accessibility of the OH groups. The DS and distribution pattern control the solubility of the CMC in water. The higher the DS, the easier to dissolve the CMC. Barba et al. (2002) have shown that the system might behave as a solution or a gel depending on the CMC concentration and the DS. Additionally, uneven distribution of the CM moieties along the polymer chain (block-like distribution of the substituents) yields a tendency towards the formation of gel and insoluble matter (Saake et al. 2000).

### 3 Materials and methods

#### 3.1 Materials

Samples from 28 different market pulps, 51 machine dried and three wet pulps collected between 2012 and 2020, were studied (Table 2). They represent the generical product groups softwood and hardwood (SW and HW) and kraft and sulfite (k and s). Some of the studied pulp products were highly pure pulps (-hp), commonly used for special applications within cellulose derivatives or high-tenacity viscose fibers. Two studied pulps were paper pulps (-paper). Remaining products were pulps used in the production of standard viscose staple fibers (VSF).

Acetic acid 95-97 %, aq. NaOH p.a., water-free sodium acetate (CH<sub>3</sub>COONa) p.a., L(+)-arabinose 99%, D-xylose 99%, D-(+)-mannose 99%, D-(+)-galactose 99%, D-(+)-glucose 99,5%, acetone p.a., BSTFA N,O Bis(trimethylsilyl)trifluoroacetamide/trimethylsilyl TMCS 99:1, dihydrocholesterole (5 $\alpha$ -cholestane-3 $\beta$ -ol), 13-methylpentadecanoic acid (anteiso-C16:0), pyridine, HNO<sub>3</sub> p.a., HCl p.a., La<sub>2</sub>O<sub>3</sub> p.a., CsCl p.a., copper ethylene-diamine solution (1.00 mol/l), LiCl, ethanol p.a., and N,N-dimethylacetamide, 99.9+%, were purchased from Sigma Aldrich (Sweden).

Sodium monochloroacetate, sodium hydroxide (NaOH), ethanol, isopropanol, and methanol as well as D<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>O were purchased from Sigma-Aldrich (Germany). HClO<sub>4</sub> was purchased from Roth (Germany).

#### 3.2 Methods

##### 3.2.1 Physical properties of pulp sheets

Grammage was determined according to ISO 536:1995.

Brightness was analyzed according to ISO 2470-1:2008 on pulp sheets prepared according to SCAN-CM 11:95.

**Table 2: 28 different market pulps used in this study and their fiber type, raw material and production process. As indicated in column “Number and condition of samples”, some pulp products are represented by more than one random sample from the drying machine, sometimes even as wet sample.**

<i>Pulp sample</i> <sup>a</sup>	<i>Fiber type</i>	<i>Process</i>	<i>Number and condition of samples</i> <sup>b</sup>
HWk 1	Short fiber	Kraft	10 DM <sup>c</sup> , 1 wet
HWk 2	Short fiber	Kraft	2 DM
HWk 3	Short fiber	Kraft	2 DM
HWk 4	Short fiber	Kraft	2 DM
HWk 5	Short fiber	Kraft	1 DM
HWk 6	Short fiber	Kraft	1 DM
HWk 7	Short fiber	Kraft	1 DM
HWk 8	Short fiber	Kraft	1 DM
HWk 9	Short fiber	Kraft	3 DM
HWk 10	Short fiber	Kraft	2 DM
HWk 11	Short fiber	Kraft	3 DM
HWk 12	Short fiber	Kraft	2 DM
HWs 1	Short fiber	Sulfite	2 DM
HWs 2	Short fiber	Sulfite	2 DM
HWs 3	Short fiber	Sulfite	1 DM
SWs 1	Long fiber	Sulfite	1 DM
SWs 2	Long fiber	Sulfite	2 DM
SWs 3	Long fiber	Sulfite	2 DM
SWs 4	Long fiber	Sulfite	1 DM
SWs 5	Long fiber	Sulfite	1 DM
SWk 1	Long fiber	Kraft	2 DM
SWk 2	Long fiber	Kraft	1 DM
SWk-hp 1	Long fiber	Kraft	1 DM
SWk-hp 2	Long fiber	Kraft	1 DM
HWk-hp 1	Short fiber	Kraft	1 DM
HWk-hp 2	Short fiber	Kraft	1 DM
HWk-paper	Short fiber	Kraft	1 DM, 1 wet
SWk-paper	Long fiber	Kraft	1 DM, 1 wet

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12)

distinguishes different commercially available pulp products.

<sup>b</sup> DM – product sample from the drying machine, different DM-samples from the same pulp product are later on distinguished by a letter suffix (a, b...); wet – wet never-dried sample for further processing in laboratory

<sup>c</sup> 10 DM – ten samples from that market pulp. Three were standard products (HWk 1a, HWk 1b, HWk 1c), two were variations of HWk-1a with elevated content of extractives (e/E) and xylan (x/X) content (HWk 1a-ex, HWk 1a-EX), five were variations of the standard product with steadily increasing intrinsic viscosity (HWk 1-282, HWk 1-349, HWk 1-403, HWk 1-463, HWk 1-532).

### **3.2.2 Cold extraction of never-dried paper pulp**

Cold extraction of the never-dried paper-pulps HWk-paper and SWk-paper was carried out at room temperature according to Lund et al. (2012) using 2.5, 4.0, and 8.0 wt% aq. NaOH. The pulps were extracted for one hour at room temperature at a pulp consistency of 5%. After completed extraction, the pulp was dewatered in a Büchner funnel and carefully washed with deionized water. Drying of the extracted and dewatered pulp (ca 24 wt%) was performed according to 3.2.3.

### **3.2.3 Lab-drying of pulp**

Some wet pulp samples were available from the wire section as fully bleached and washed, never-dried samples before entering the press section. Different finishing procedures were applied to a range of dry contents:

- a) Wire drained: Conservation of the dry content as derived from the wire section or the funnel (3.2.2) was achieved by sealing a couched sample-cake (370 g/m<sup>2</sup>) in a plastic bag.
- b) Pressed: Pressing of a couched sample-cake from section a) in a lab-press and conservation of the dry-content (ca 50 wt%) by sealing the pressed sample-cake in a plastic bag. Pressing was conducted at 400 kPa for less than 5 minutes with a surplus of blotting paper on both sides of the sample-cake.
- c) 23°C/50% r.h.: Free air-drying of a pressed sample-cake from section b) at 23 °C and 50 % relative humidity until stable dry-content was reached.

- d) 103°C/0% r.h.: Free oven-drying of the pressed sample from section b) at 103 °C and constant ambient pressure until stable dry-content was reached.
- e) 90°C/50% r.h. (1h): Free drying in a climate chamber at 90 °C and 50 % relative humidity under an hour.
- f) 90°C/50% r.h. (12h):Free drying in a climate chamber at 90 °C and 50 % relative humidity under 12 hours.

#### **3.2.4 Production of alkali cellulose (AC), regenerated alkali cellulose (rAC), press lye and analysis of the alkali resistance of pulps**

Alkali resistance (ISO 699:2015) of the pulps was determined as the R-value. The samples were either dried on an industrial drying machine or according to 3.2.3 e). Residues for further investigations were produced with 10, 14 and 17 - 20 wt% aq. NaOH at 20, 35 and 44 - 50°C. No further modifications from the standard procedure, ISO 699:2015, had to be considered when the alkali concentration was altered. When applying temperatures >30°C, a finer glass filter (40 – 100 µm) had to be used to compensate for the lower intrinsic viscosity of the liquid. The residue (R) was regenerated alkali cellulose (rAC) and was used for further investigations.

The results presented in 4.2.1, 4.2.6 and 4.2.7 were determined on rAC and press lye from AC produced under mill-like conditions. Some 30 g of pulp (calculated as oven dry) were dispersed in 900 g lye (18 wt% aq. NaOH) at 50 °C for 30 min under steady and moderate agitation. The sheet alkalization presented in 4.2.1 was simulated by soaking two stacked pulp sheets (ca 10 g) with a diameter of 8.5 cm (calculated as oven dry) with 375 g lye (18 wt% aq. NaOH) for 40 min – no agitation was applied. The respective reference for slurry alkalization was performed using the same conditions, but agitating the sample steadily and moderately. All pulp slurries and pulp stacks were dewatered through a nylon wire (pore width 70 µm) aiming for a press-out factor of 2.6 and an alpha-cellulose content of 36 wt%. The press-out factor is the quotient of pressed weight of the AC and dry weight of the pulp-input. The press-lye was kept for further analysis. Determination of the alkali content and the alpha-cellulose

content as well as the regeneration of the AC was performed according to Zellcheming Merkblatt III/5, version 1953.

### **3.2.5 Analysis of pulps and regenerated alkali cellulose (rAC)**

The carbohydrate composition was analyzed via acid hydrolysis (SCAN-CM 71:09) using 72 wt% aq. H<sub>2</sub>SO<sub>4</sub>. The acid-insoluble Klason lignin and acid-soluble lignin were determined, and the rest of the sample was assumed to be carbohydrates. The content of Klason lignin was determined gravimetrically. The content of acid-soluble lignin was determined from the hydrolysis filtrate after the removal of Klason lignin using UV spectroscopy at 205 nm, assuming an absorptivity factor of 113 dm<sup>3</sup> g<sup>-1</sup> cm<sup>-1</sup> for hardwood pulps and 128 dm<sup>3</sup> g<sup>-1</sup> cm<sup>-1</sup> for softwood pulps. The liberated neutral monosaccharides in the hydrolysis filtrate were quantified using High-Performance Anion-Exchange Chromatography (HPAE ICS-3000 Dionex with Pulsed Amperometric Detection (PAD)) and reported as anhydrous carbohydrate according to SCAN-CM 71:09.

The content of extractives was determined with extraction in a Soxhlet apparatus using acetone followed by drying at 105 °C based on SS-EN ISO 14453:2014.

Metal ions were determined with ICP-OES according to SCAN-CM 38, and ash content was determined according to ISO 1762.

Fiber properties were analyzed according to ISO 16065-2:2014 with unpolarized light using a Lorentzen & Wettre Fiber Tester by automated image analysis of the fibers suspended in water. Fines content is given as a length-weighted portion of particles shorter than 200 µm.

The water retention value WRV was determined according to SCAN-C 62:00 by applying a centrifugal force of 3000 g for 15 min. The results were reported as [g H<sub>2</sub>O/g solids].

Intrinsic viscosity  $\eta$  (limiting viscosity number) was analyzed according to ISO 5351:2010 based on the dissolution of the sample in copper ethylene-diamine solution (CED).



Molecular weight distribution was determined using GPC-MALS (solvent DMAc/LiCl) according to Henniges et al. (2011) on the following equipment: an RI detector (Waytt) Optilab T-rEX, a Multi Angle Light Scattering Detector (Waytt) Down Heleos II (658 nm), four columns (photoluminescence gel mixed A LS, 0.20  $\mu\text{m}$ , 7.5 x 300 mm) from Agilent. Data processing was done in Astra6 to calculate key values such as the weight-average degree of polymerization (DP<sub>w</sub>, DP), the polydispersity index (PDI), and the weight fraction of molecules with DP <100. The correlation to the intrinsic viscosity with  $R^2 = 0.89$  is given as

$$DP = 4.1287 \eta - 525.44 \quad \text{Equation 2}$$

The crystallinity, ratio of cellulose I / II and partly the crystallite dimensions were determined with wide-angle X-ray scattering (WAXS), solid state NMR and Raman spectroscopy.

Wide-angle X-ray scattering (WAXS) was performed with a Bruker D8 Advance (CuK $\alpha$ -Dublett,  $\lambda = 1.54184 \text{ \AA}$ , transmission), diffractogram recording  $8^\circ \leq 2\theta \leq 105^\circ$  according to DIN EN 13925-1...3. The crystallinity index (CI) was calculated according to Ruland and Vonk as summarized in Krässig (1993) using the amorphous subtraction method. Cellulose I (Cell I) was calculated according to Schurz et al. (1987) and cellulose II (Cell II) was calculated according to Lenz et al. (1986). The crystallite dimensions were calculated via crystallite size equivalents from peak width  $w$  and peak position  $\theta$  using the Scherrer Equation (Scherrer 1918).

$$D_{hkl} = \frac{0.89 \lambda}{w \times \cos\theta} \quad \text{Equation 3}$$

$D_{hkl}$  is the crystallite size estimated from the (hkl) line,  $\lambda$  is the X-ray wavelength, and  $\theta$  is the diffraction angle.

CP/MAS  $^{13}\text{C}$ -NMR spectra were recorded at RISE Research Institutes of Sweden, Stockholm, with a Bruker Advance III AQS 400 SB instrument operating at 9.7 T, fitted with a double air-bearing two-channel probe head. Dry pulp samples were rewetted in H<sub>2</sub>O for 24 h, and vacuum filtrated through a polyester filter (5 $\mu\text{m}$ ) on a Buechner funnel. Wet samples, corresponding to 150 mg dry matter each, were packed uniformly in a 4 mm zirconium oxide rotor. All measurements were performed at  $296 \pm 1 \text{ K}$ . The MAS rate was 10 kHz.

Acquisition was performed with a CP pulse sequence using a 2.95  $\mu\text{s}$  proton 90° pulse, an 800  $\mu\text{s}$  ramped (100 – 50 %) falling contact pulse and a 2.5 s delay between repetitions. A SPINAL64 pulse sequence was used for  $^1\text{H}$  decoupling. Harman-Hahn matching procedure was performed on glycine and the chemical shift scale was calibrated to TMS ( $(\text{CH}_3)_4\text{Si}$ ) by assigning the data point of maximum intensity in alfa-glycine carbonyl signal a chemical shift of 176.03 ppm.

CI was determined using the C4 peak separation method according to Wickholm, Larsson and Iversen (1998). Cell II was determined according to Olsson, Idström, Nordstierna and Westman (2014) and was calibrated towards WAXS by applying the rate between Cell I and II as determined by WAXS for the sample *SWk-hp 1*. The specific surface area  $SSA_{LFAD}$  [ $\text{m}^2/\text{g}$ ] was determined according to Larsson, Wickholm, Iversen (1997) using the equation 4 where the lateral fibril diameter LFAD [nm] was determined by NMR-analysis.

$$SSA_{LFAD} = \frac{2652}{LFAD} \quad \text{Equation 4}$$

NIR FT Raman spectroscopy was performed using a MultiRam III (Bruker) with a liquid-nitrogen-cooled Ge diode as the detector. A Nd:YAG laser (1064 nm) with a maximum power of 500 mW was the light source for the excitation of the Raman scattering. Power of 200 mW was used for the measurement. Because of the solid and compact structure of the residues, no further sample preparation was necessary. A total of eight points per sample was measured. Each point was measured 100 times. The data was collected and analysed using OPUS software. All spectra of one sample were combined into one, and this averaged spectrum was then handled with OriginPro. CI was calculated according to Schenzel et al. (2005). Cellulose II was calculated according to Agarwal (2017) and Schenzel (2009). Amorphous cellulose was calculated according to Agarwal (2017).

The Fiber saturation point (FSP) was measured at RISE Research Institutes of Sweden, Stockholm, by solute exclusion technique according to Stone and Scallan (1967) using a large macromolecule (dextran of 2000 kDa with a hydrodynamic diameter of ca 100 nm; Larsson et al. 2013). The results were reported as the dimensionless ratio of the mass of the fiber pore water inaccessible for the added macromolecule divided by the dry solid mass of the

fibers (g/g). Accordingly, the fiber pore water represented the volume of pores < 100 nm in diameter. Combining the specific surface area measured by the NMR method and FSP made it possible to calculate the average fiber wall pore sizes (Larsson et al. 2013).

### **3.2.6 Analysis of press lye**

The carbohydrate composition was analyzed via acid hydrolysis (similar to SCAN-CM 71:09) using 72 wt% aq. H<sub>2</sub>SO<sub>4</sub>. Initial neutralization of the lye was done with 5 M HCl. The liberated neutral monosaccharides in the hydrolysis filtrate were quantified using High-Performance Anion-Exchange Chromatography (HPAE ICS-3000 Dionex with Pulsed Amperometric Detection (PAD)) and reported as anhydrous carbohydrate in mg/kg lye.

### **3.2.7 Preparation of carboxymethyl cellulose (CMC)**

5 g dry-ground pulp (0.1 mm screen) was suspended in 117 g isopropanol, and 2.09 g NaOH was added as 3, 5, or 15 wt% aqueous solution. The reaction mixture was stirred in a reaction vessel with heating jacket and condenser at room temperature for 1 h. Then, 6.10 g sodium monochloroacetate (SMCA) was added, and the reaction took place for 5 h at 55 °C under stirring. After cooling to room temperature, the product was precipitated in 800 ml 80 % (v/v) aqueous methanol, neutralized with diluted acetic acid, and washed four times with 400 ml 80 % ethanol and dried in a vacuum at 40 °C.

### **3.2.8 Analysis of carboxymethyl cellulose (CMC)**

The degree of substitution (DS) of carboxymethyl groups was determined after complete hydrolytic chain degradation using HPLC according to Heinze et al. (1994 and 1999) and <sup>1</sup>H NMR spectroscopy (Baar et al. 1994). For HPLC, the samples were hydrolyzed with 70% (v/v) HClO<sub>4</sub> for 10 min at 25 °C and after dilution with a nine-fold amount of water for 16 h at 100 °C. After careful neutralization with 2 M aqueous KOH solution, the sample was kept at 4 °C for 1 h (to guarantee the complete precipitation of KClO<sub>4</sub>, which was separated by filtration) after which the solution was reduced to ~ 5 ml. The samples (20 µl)

were analyzed using HPLC (JASCO): two Bio-Rad Aminex HPX-87 H columns, an intelligent HPLC pump (PU-980), an RI detector (RI-930), and an HPLC software (BOR-WIN). The total error margin was DS +/- 0, 05. For  $^1\text{H}$  NMR spectroscopy, the samples were hydrolyzed with 25%  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  for 5 h at 90 °C. The analyses were carried out with a 250 MHz spectrometer (Bruker, WP250) at room temperature.

The viscosity of the CMC was measured using a 1 wt% aqueous solution with a Brookfield RV at 23 °C.

Insoluble matter (including gels) was gravimetrically determined as residue from the 1 wt% aqueous solution. In order to separate insoluble matter and the gel fraction from the soluble fraction, the solution was centrifuged (15 min at 3 000 g). The upper fraction was decanted and filtrated through a 5  $\mu\text{m}$  polycarbonate filter using a vacuum. The bottom fraction was subsequently diluted in excess of water followed by centrifugation, decantation, and filtration. This procedure was repeated up to three times until no bottom fraction was visible, and the whole sample had passed through the filter, or until the bottom fraction was clearly visible as an unfilterable gel fraction. The filter with residue and, optionally, the unfilterable gel fraction were oven dried and weighed.

### **3.2.9 Data modelling**

The software tools used for data modelling were Modde12.1 (Umetrics/Sartorius, Göttingen, Germany), and JMP®14.0 (SAS Institute, Cary, North Carolina, USA).

## 4 Results and discussion

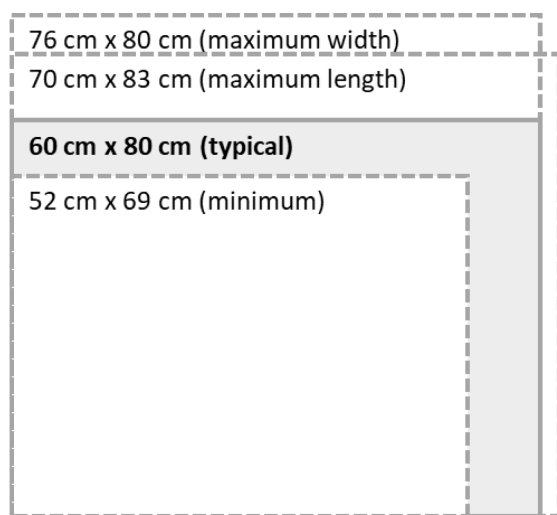
### 4.1 Deviation of properties of dissolving pulps

Key parameters of dissolving pulp products are usually communicated in confidential product specifications. This study illustrated the diversity of dissolving wood pulp (DWP) products globally available by evaluating 44 different pulp samples from 27 commercially-available pulp products collected since viscose production soared in the 2010s. Most of the pulp products investigated were destined for use in commodity viscose staple fiber (VSF). The VSF-pulps were further categorized by their raw material (hardwood (HW) or softwood (SW)) and production process (kraft (k) or sulfite (s)) as HWk, HWs, SWs and SWk. Some high-purity pulps for production of viscose with higher demands on mechanical properties (-hp) as well as a paper pulp (-paper) were included with the intention of placing the evaluation of the VSF-pulps within a wider context. All analysis data are included in the appendix (Table 12 - Table 16).

#### 4.1.1 Pulp sheet properties

All investigated pulps were industrially finished as sheets. Sheet dimensions were typically 60 x 80 cm<sup>2</sup>. The smallest measured 52 x 69 cm<sup>2</sup>, the largest measured 76 x 80cm<sup>2</sup> and 70 x 83 cm<sup>2</sup> (Figure 7). Both the VSF-mill and the DWP-producer have limited possibilities to adapt to different sheet dimensions due to limited adjustability of their production and feeding equipment. Bone-dry grammage of the sheets was ca 650 – 1200 g/m<sup>2</sup>.

Pulp brightness reflects the functionality of the bleaching line and the purity of the pulp. The raw material and the process establish the base line for generic pulps. Sulfite pulps are easily bleached to >92 %ISO. This level was reached for the most investigated sulfite pulps and even for some kraft pulps.



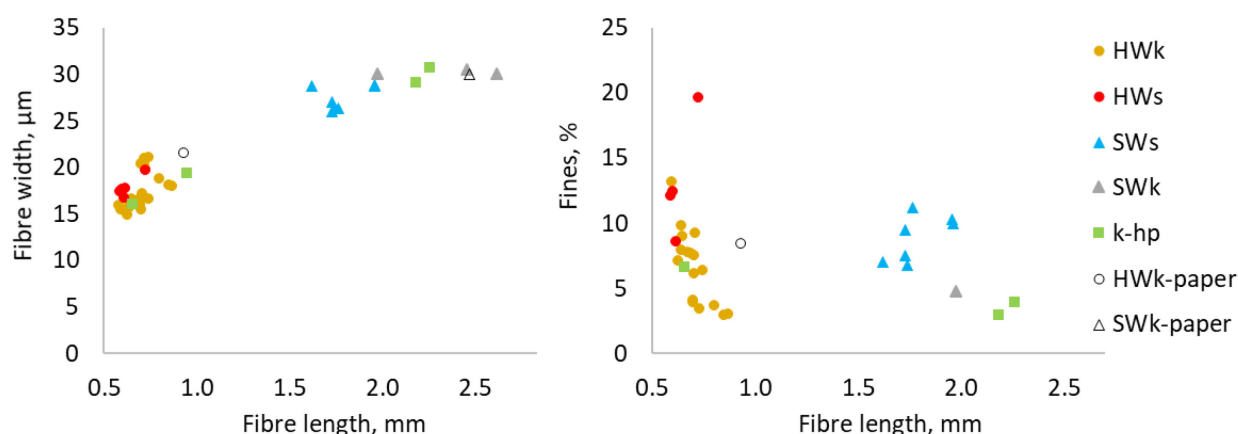
**Figure 7: Dimensions of commercially available dissolving wood pulp sheets. Extreme measures have dashed lines.**

#### 4.1.2 Fiber morphology

Commonly, specific fiber morphology is not connected to the properties of dissolving wood pulp. At least as long as the undissolved fibers are treated in the viscose process, fiber morphology of the pulp is an important factor from a techno-mechanical point of view, and it is therefore important to examine the possible variation among today's market pulps. Most obviously, it influences, among other pulping process factors, the ease with which the sheet is disintegrated, depending on fiber length. The influence of fiber length and fines content on the pressability of the alkali cellulose slurry was described by various authors in the 1950-60s and summarized by Götze (1967). Pressing aims for fast drainage to the target press factor at minimum yield loss and maximum purification. The procedure consists of two phases. The first – and usually the bottleneck of the equipment - is dominated by free drainage in the vat and it has been stated that long fibers perform better. The less critical second phase of drainage under linear load has been shown to perform better with short fibers (Laamanen and Sihtola 1962). Fines (defined as particles which pass through a 55  $\mu\text{m}$  wire) have been shown to decrease process yield and retard pressing by blocking sieve openings (More 1962, Treiber et al. 1958). Accordingly, even the composition of the press lye will be influenced by the particle size distribution of the pulp. One wonders if existing process equipment is able to freely adapt to the existing span of fiber properties among the available pulp products in

terms of feeding velocities and forces, agitator geometry, pressure and pore sizes applied. No research evolving these aspects was found.

The fiber length of the investigated market pulps was below 1.0 mm or above 1.5 mm for hardwood and softwood pulps, respectively (Figure 8, left). The combination of fiber length and width made it possible to provide an indication of the wood species used in the product. The cluster of the hardwood pulp with longer and coarser fibers might primarily be produced from birch, beech and poplar. The shorter and more narrow fibers (fiber width < 18  $\mu\text{m}$ ) might be related to hardwoods such as various subspecies of eucalyptus, acacia, aspen and maple (Ilvessalo-Pfäffli 1994, Hillman 1999). The fiber width of the softwoods varied depending on the species and provenience. The wide variation of fiber length could be explained by the applied process with sulfite pulping resulting in a lower fiber length and an elevated fines content (Figure 8, right; 2.1.3). The tendency for more fines in sulfite pulp, measured as particles shorter than 200  $\mu\text{m}$ , was less clear for the hardwood pulps where some kraft pulps with small and narrow fibers contained more fines than a hardwood sulfite pulp.



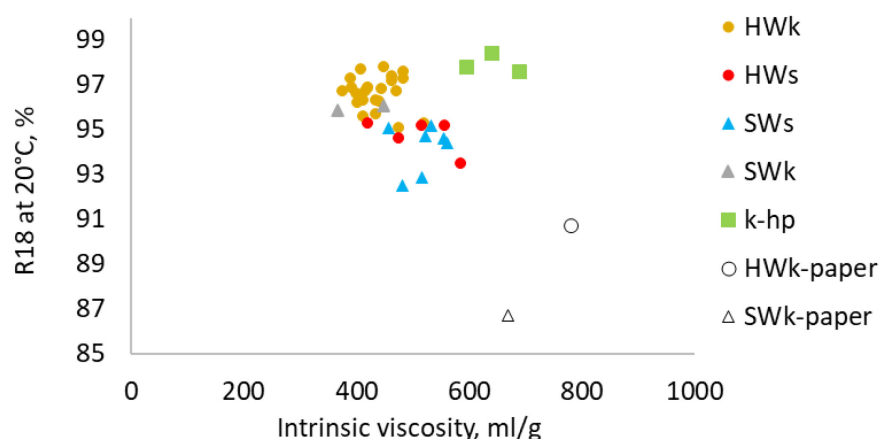
**Figure 8: Fiber morphology of different dissolving pulps and two paper pulps (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity)**

#### 4.1.3 Carbohydrates

Figure 9 illustrates the most important characteristics of a dissolving pulp, intrinsic viscosity and R18. Intrinsic viscosity is a measure for the mean degree

of polymerization in the pulp and its value is adapted to the demands of the viscose product in question. Viscose processes which use lower pulp viscosities can dissolve at more economical conditions but deliver primarily spun fibers at lower tenacity. Due to pulping process conditions, sulfite pulps are characterized by low R18 and kraft pulps by high R18 (2.1.3).

Investigated market kraft pulps for use in VSF (HWk, SWk) had a typical R18 of 95.5 – 98.0 % and were delivered at an intrinsic viscosity of 380 – 480 ml/g (Figure 9). Their high-purity version for use in high quality viscose fibers (k-hp) had a R18 of 97.5 – 98.5 % at a viscosity of 600 – 700 ml/g. The investigated sulfite pulps used in VSF had a significantly lower R18 than the kraft pulps (< 95 %), but only a few of them were as low as 92.0 – 93.0, which is the level given in literature (Table 1). The viscosity for VSF-application was found to be 420 – 560 ml/g, which was significantly higher than kraft pulps for the same application.

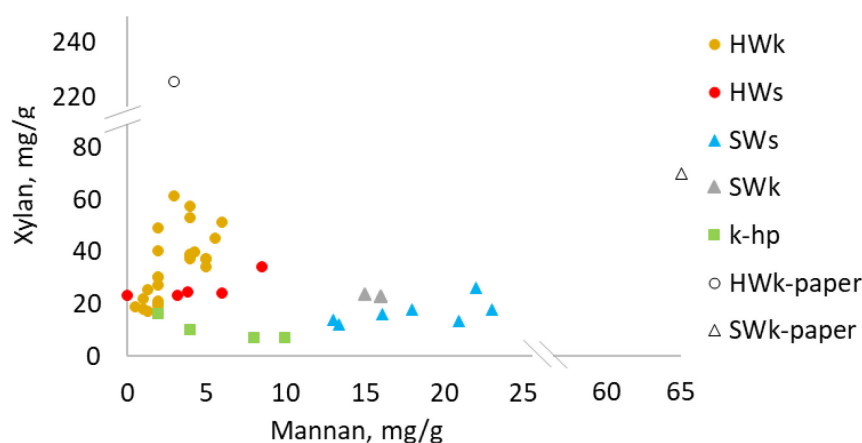


**Figure 9: R18 and intrinsic viscosity of different dissolving pulps and one paper pulp (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity)**

Due to the chemical composition of the raw material, hardwood pulps contain higher amounts of xylan and softwood pulps higher amounts of mannan (2.1.3). The purest softwood pulps (among k-hp) contained less than 11 mg/g mannan, while SWk contained ca. 15 mg/g mannan and SWs up to 23 mg/g mannan (Figure 10). This comparably high content of mannan in SWs is due to the acid process conditions. The xylan content of all investigated softwood pulps was on the low level of 7 – 26 mg/g. The data for the dissolving pulps can be compared



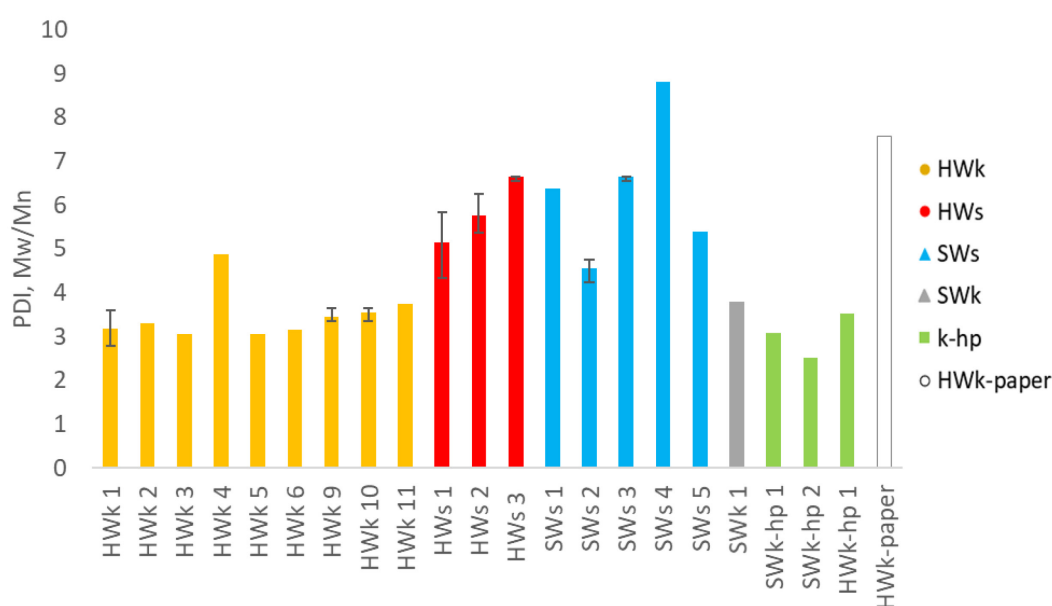
with SWk-paper – a pulp processed with focus on preserving the hemicelluloses – were 65 mg/g mannan were left in the pulp. Mannan in hardwood pulp is generally low due to the low initial content in the raw material. One of the acid cooked HWs contained 9 mg/g mannan, HWk did contain a maximum of 6 mg/g mannan. Xylan content could be shown to vary in HWs between 23 and 34 mg/g. This is a moderate variation on a medium level. HWk varied between 17 and 61 mg/g, hardwood for high-purity applications (among k-hp) had the lowest xylan content with 10 mg/g – but not as low as their softwood equivalent. This demonstrated that big differences in the raw material can still be found after comprehensive chemical processing. Data from the latest literature (Duan et al. 2015) fit in the range presented from this study. The data for the dissolving pulps can be compared with HWk-paper – a pulp processed with focus on preserving the hemicelluloses – where more than 200 mg/g xylan were left in the pulp. The fact that several HWk contained more mannan than HWk-paper is surely explained by the high yield of the paper pulp, reducing the relative share of the mannan left in the pulp.



**Figure 10: Hemicelluloses mannan and xylan in different dissolving pulps and two paper pulps (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity)**

From literature it has been clear that sulfite pulps have a broader molecular weight distribution compared to the kraft pulps (2.1.3). The pulps investigated in this study confirmed this tendency (Figure 11). A rough classification of PDI

for the investigated generic pulps could be given as  $k\text{-hp} \leq 3.5$ ,  $k\ 3 - 4$ ,  $s > 4.5$  and paper  $> 7$ . Accordingly, the sulfite pulps studied had a high content of material  $DP < 100$  and  $DP > 2000$ , the standard dissolving kraft pulps (HWk and SWk) had a low content of material with  $DP < 100$  and the high-purity kraft pulps (k-hp) had an even lower content of material with  $DP < 100$  together with the highest content of material with  $DP > 2000$  (Appendix Table 15). The high PDI of HWk-paper can be explained by the combination of a comparably high DP combined with the highest level of xylan.

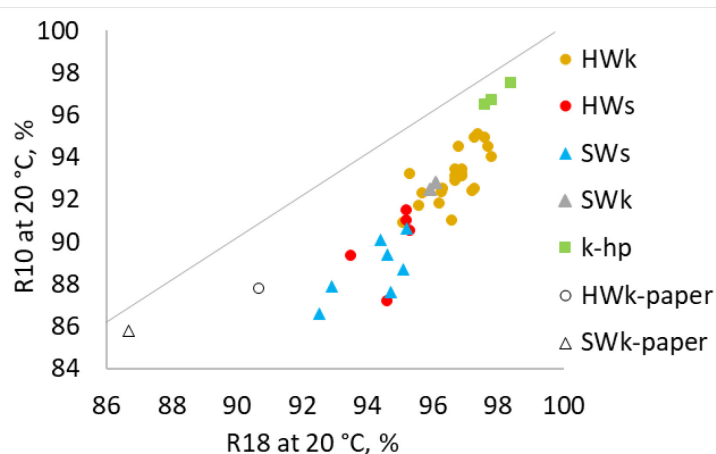


**Figure 11: Polydispersity index (PDI) as quotient of mass-average molar mass and number-average molar mass of different dissolving pulp products and one paper pulp (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity). The span for the minimum and maximum value is given in those cases, where two or more samples were measured for respective pulp product.**

While R18 is a central property due to common viscose steeping conditions, R10 is of interest as wood pulps are supposed to reach maximum solubility at 10 wt% caustic soda. Hence, the residue at 10 wt%-extraction is smaller than at 18 wt% (2.1.2) since a higher amount of low molecular weight material in the pulp, consisting of both hemicelluloses and cellulose, will be extracted. Accordingly, sulfite pulps (HWs, SWs) had the lowest R10-values ( $\leq 91.5\%$ ) and high-purity pulps (k-hp) the highest R10-values ( $\geq 96.5$ ) (Figure 12). Even the paper pulps

had low R10. This is despite a low content of material with  $DP < 100$  (HWk-paper), which is on the same level as that for HWk and SWk (Appendix Table 15). The explanation for this low R10 might be found in the high content of hemicellulose (Figure 10).

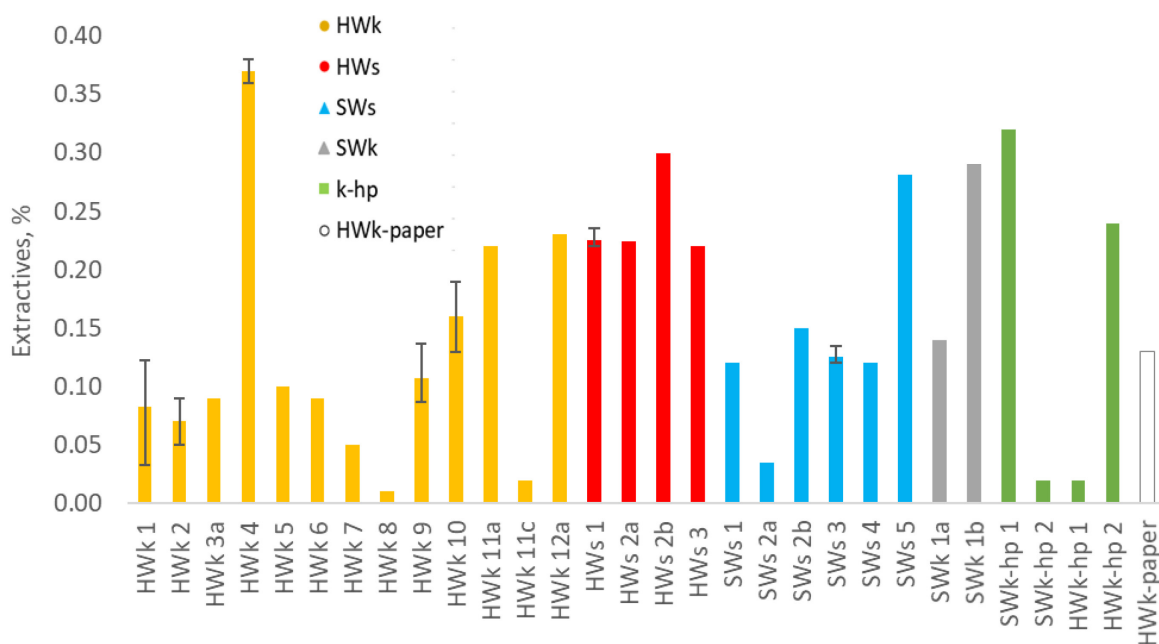
Using equation 1 (2.1.2), the data from this study proposed alpha contents of the different generic pulps of 94 – 96 % for kraft pulps, 90 – 93 % for sulfite pulps and  $> 97$  % for high-purity pulps (Appendix Table 14). These data were in accordance with the latest literature (Duan et al. 2015).



**Figure 12: R10-value in dependence of the R18-value for different dissolving pulps and two paper pulps (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity)**

One would assume that the smaller the quotient  $R18/R10$ , the narrower the molecular weight distribution (PDI) of the pulp. Sixta (2006b) has shown the difference between  $R10/20$  and  $R18/20$  to be a measure for the low molecular weight cellulose fraction, where a large difference has indicated a wide PDI. The data from this study could not support these assumptions (Table 14 and Table 15). A correlation to PDI determined by GPC-MALS (GPC) and the  $R18/R10$ -quotient was only given between, but not within the generic pulp groups (Figure 13). The absent correlation might be due to the wide variety of pulps with differing intrinsic viscosity levels and process histories. Thus, the fractions of the different pulps were alkali resistant to different degrees. Different alkali resistance of pulp components will change the ranking of remaining residue from the pulps when extracting with alkali under different conditions (4.2.5).

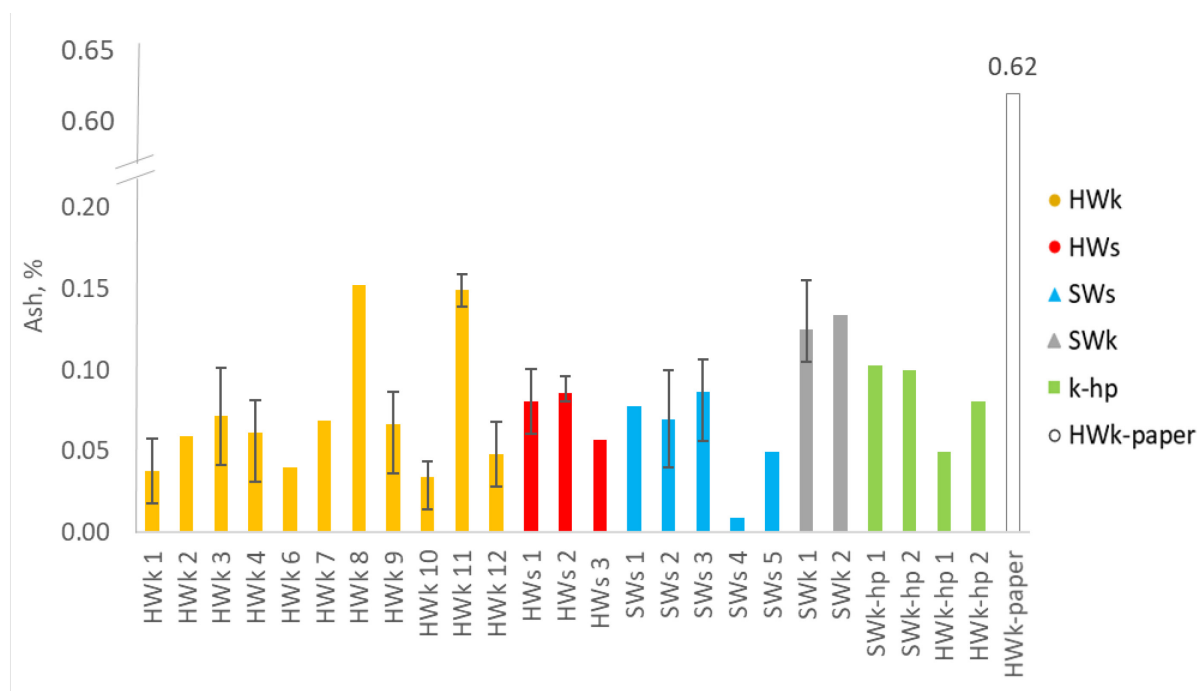




**Figure 14: Acetone extractives of different dissolving pulp products and one paper pulp (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity). The span for the minimum and maximum value is given in those cases, where two or more samples were measured for respective pulp product.**

#### 4.1.5 Mineral matters

Ash is the gravimetric sum of the oxidized metals in the pulp. Silica (Si) and calcium (Ca) are mainly derived from the wood, while magnesium (Mg) and sodium (Na) are added with the process chemicals. The transition metals copper (Cu), manganese (Mn) and iron (Fe) reflect the water quality on the production site. According to Figure 15, most dissolving pulps had an ash content below 0.1 %. A few reached levels of  $\leq 0.05$  %. Some kraft pulps exceeded the 0.1 %-limit. The sixfold higher ash content in the included paper pulp, where ash content is no issue, illustrated that dissolving pulp production successfully forces those low levels of ash content. Extended washing of the pulp and use of demineralized water at the drying machine are strategies to decrease the metal content in pulp.



**Figure 15: Ash content of different dissolving pulp products and one paper pulp (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity). The span for the minimum and maximum value is given in those cases, where two or more samples were measured for respective pulp product.**

It should be noted that no correlation between ash content and the sum of the different commonly-analyzed metals was found (Appendix Table 16). As metals influence the preripening of alkali cellulose and might cause precipitation in the process line, they must be controlled in the pulps used for viscose.

HWk-pulps especially stood out with elevated contents of metals.

Seven out of 12 HWk-products had Si-contents higher or partly higher than 20 ppm. Among SWs two out of five products had higher or partly higher Si-contents. The Si-content in *HWk-paper*, where no attention is paid to minimize the metal content, was 682 ppm.

Ca over 50 ppm was found in four out of 12 HWk-, one in three HWs- and one in five SWS-products. The Ca-level of *SWs5* was as high as in *HWk-paper* (> 300 ppm).

One *SWs*-product had a highly elevated content of Mg (243 ppm), which was one in three of the content found in *HWk-paper*. Some sulfite processes are Mg-

based, which might be the reason for the high content in *SWs1*. All other pulps had a Mg-content < 60 ppm.

Fe was found to be > 6 ppm in five out of 12 HWk-products and one out of five SWs-products. *HWk 4b* had twice the content of Fe than *HWk-paper*.

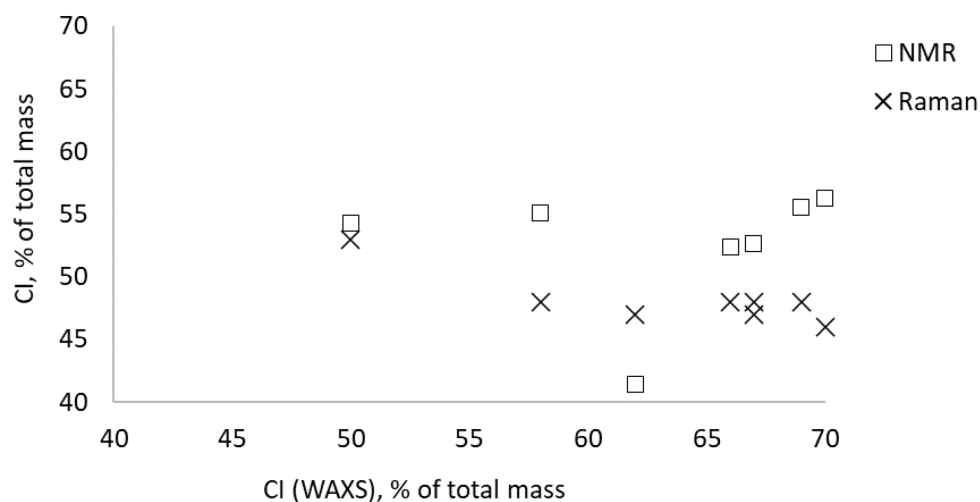
Cu was on the low level of  $\leq 1$  ppm for all the pulps analyzed.

In three analyzed DWP-samples, Mn was found to be > 0,5 ppm. All of these samples were different HWk-products. At 2 ppm, one sample was found to exceed even the level found in a paper pulp and also had a clearly elevated ash content (0.15 %).

#### **4.1.6 Crystallinity and crystallite dimension according to different methods**

This study determined supramolecular properties of different pulps using the techniques of wide-angle X-ray scattering (WAXS), CP/MAS  $^{13}\text{C}$ -NMR (NMR), and NIR FT Raman spectroscopy (Raman). Eight generically-different pulps were studied. The results for crystallinity index (CI), cellulose I (Cell I), cellulose II (Cell II) and the crystallite dimensions determined as lateral fibril diameter (LFD) or crystallite width, height and length are given in the appendix, Table 17. The scattering patterns and spectra from the three measurement techniques applied for all pulps are given in the appendix, Figure 51 - Figure 53.

According to WAXS, crystallinity was ca 50 – 70 % for the tested market pulps (Figure 16). Using NMR, CI for the same samples were on a level of ca 40 – 55 % and Raman determined CI to be ca 45 – 55 %. The fact that no correlation could be seen between the different measurement techniques for the generically-different pulps, representing material with different carbohydrate composition and process history, emphasizes the fact that all techniques quantify different details of the phenomenon crystallinity.

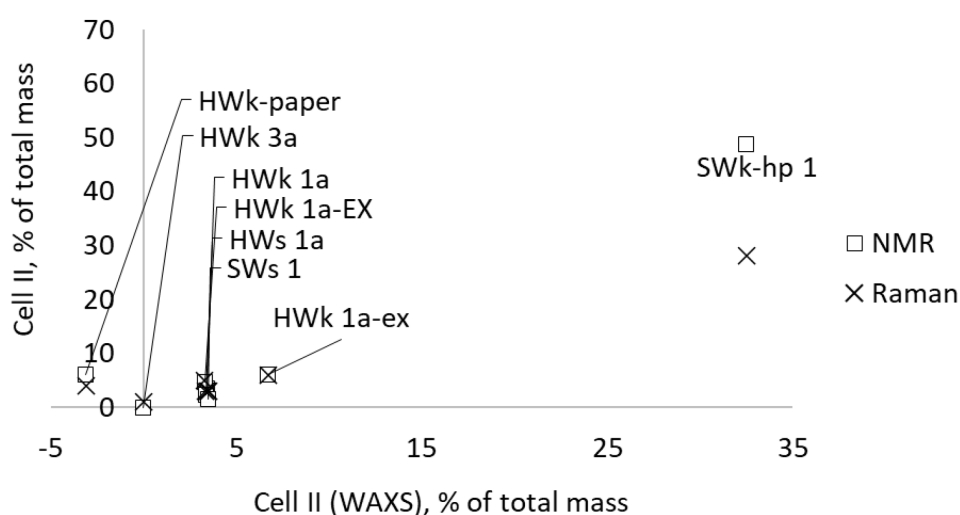


**Figure 16: Crystallinity index (CI) of different generic pulps measured with CP/MAS 13C-NMR spectroscopy, X-ray scattering (WAXS) and NIR FT Raman spectroscopy**

A more distinct correlation between WAXS, NMR and Raman could be found for the content of the allomorph cellulose II (Cell II) in the tested pulps (Figure 17). It could be shown that commodity dissolving wood pulps (DWP), destined for the use in viscose staple fibers (VSF), had a content of Cell II of 0 to <10 %. Assuming a significance of the determined Cell II-content of  $\pm 5\%$ , it could be concluded that many commodity DWP comprise some minor volumes of structures to be related to this allomorph. The kraft process exposes the fibers to alkaline conditions during long periods of time. But, the abundance of Cell II could not be related to the generic process. Neither standard kraft nor sulfite pulping process settings reach alkali concentration  $\geq 8$  wt% aq. NaOH where phase transition to sodium cellulose (Na-Cell) is known to start to take place to a large extent (2.3.1). Three levels of Cell II could be detected for the commodity DWP. One hardwood kraft pulp (*HWk 3a*) contained no detectable amounts of Cell II, two variants of *HWk 1a* and two sulfite pulps (*HWs 1a* and *SWs 1*) contained between 0-5 % Cell II and a third variant of *HWk 1a* contained above 5%. Unknown details in the processes are supposed to cause these differences. *SWk-hp 1*, which is a highly pure specialty DWP of high DP and applied in the production of cellulose derivatives, could be shown to contain distinct amounts of Cell II measured to 30-50 % depending on the method used. This implies that the purity was created by alkaline treatment in order to extract short-chained



polymers. Cold alkaline extraction is a known method for upgrading DWP to highly-pure specialty grades. Typical process settings are 4.6–10.8 wt% aq. NaOH at 20–40 °C (Sixta 2006a). Translating the measured Cell II content in *SWk-hp 1* according to Fink et al. (1982) the pulp was assumingly treated and purified with an alkali concentration of ca 12 wt% aq. NaOH (2.3.1). This exceeded the typical process settings given by Sixta (2006a), though it is supported by Rydholm (1965) who has stated that concentrations of 10–12 wt% aq. NaOH applied at room temperature are most efficient to remove short-chain material from the pulp.



**Figure 17: Cellulose II (Cell II) in different generic pulps measured with CP/MAS  $^{13}\text{C}$ -NMR spectroscopy, X-ray scattering (WAXS) and NIR FT Raman spectroscopy (SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, the cipher code represents different pulp products according to Table 2, ex/EX - high extractives and xylan (ex < EX))**

The magnitude for the crystallite dimensions was ca 4 - 6 nm measured as LFD by NMR and crystallite width and height by WAXS. This is within the common range of data given in literature (Duan et al. 2015, Sixta 2006b, Testova et al. 2014). WAXS-data as reported by Duan et al. and Sixta have indicated slightly smaller crystallite dimensions for sulfite dissolving pulp. This slight trend could be confirmed by the present data measured with NMR (sulfite pulps 4.5–4.6 nm; kraft pulps 4.7–5.5 nm). For *SWK-hp 1* and *HWk-paper* it was not seen as possible to calculate a reliable LFD from the NMR-data as the mixed lattices of Cell I and

Cell II or the abundance of a high amount of xylan were resulting in overlapping peaks which made a deconvolution arbitrary. However, the WAXS-data made a mathematical reliable deconvolution for the different phases possible, which resulted in dimensions for each crystalline lattice (Appendix, Table 17). In any case, the dimensional data calculated from WAXS showed neither distinct differences between the pulps, nor expected tendencies. Presumably, the reflexes from the measurements were too weak to allow this kind of data evaluation.

## **4.2 Alkali treatment of wood pulps**

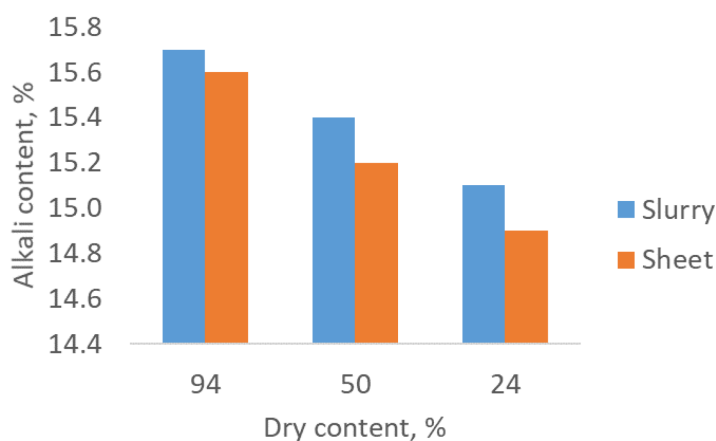
Different studies investigating the action of alkaline extraction, so-called alkalization, on pulp in general and on different pulps are presented in this chapter. Parameters elaborated are the technique of exposing the pulp for aqueous alkali (see 4.2.1), the initial intrinsic viscosity of the pulp (see 4.2.2) and the influence of the properties of the aqueous alkali used for treatment, i.e. temperature and concentration of NaOH (see 4.2.3 and 4.2.4). Moreover, a model was built to predict the residue of pulp after alkaline extraction at most commonly used full-scale conditions (see 4.2.5) and the effect on the non-saccharides and the composition of the press lye is discussed when treating different pulps at standard conditions (see 4.2.6 and 4.2.7).

### **4.2.1 Treatment as slurry and in sheets**

Commonly, alkalization is done by defibrating the dissolving pulp in a pulper filled with tempered aqueous alkali. Even sheet alkalization, which was standard in former times, still occurs in some processes and in laboratory procedures. Here, entire pulp sheets are soaked in lye as vertical stacks and vertically pressed together after fulfilled treatment time.

To evaluate the performance of both techniques, the alkali treatment of pulp as sheets and as pulp slurry was performed during the limited time span of 30 minutes on a series of pulps (*HWk 1*, DM and wet) with different dry contents. The lower dry contents were adjusted according to 3.2.3 a and b, the dry pulp was directly taken from the drying machine.

In every case, slurry alkalization led to a slightly higher alkali content in the pressed alkali cellulose (AC) (Figure 18). This phenomenon can be explained by the shortened time for reaching a concentration equilibrium between fiber and fluid when agitating. All further investigations in this work were performed using slurry alkalization.



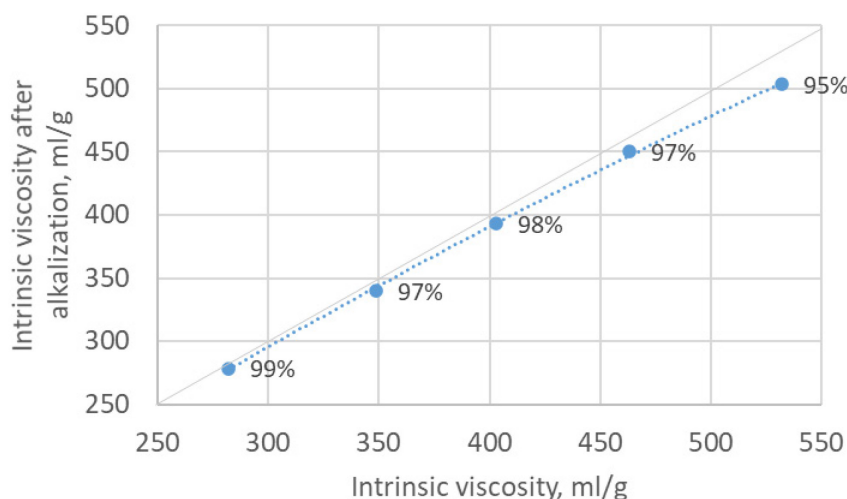
**Figure 18: Alkali content in pressed alkali cellulose produced from pulp with different dry content alkalized in 18 wt% aq. NaOH using the technique of slurry and sheet alkalization.**

The trend for decreasing alkali content in AC produced from less dry pulp is based on the fact that all samples were treated with the same absolute amount of 18 wt% aq. NaOH. This resulted in a reduced effective alkali concentration of 17.6 wt% for the sample with a dry content of 50 %, and 16.7 wt% aq. NaOH for the sample with a dry content of 24 %. Taking this into account it can be stated that the relative uptake of alkali was significantly higher in the sample with a dry content of 24 %. This might be explained by the initially more swollen structure of that sample also shortening the time for reaching a concentration equilibrium.

It is assumed that slurry alkalized AC, pressed and fluffed, will depolymerize faster to a lower intrinsic viscosity during a certain time. This faster aging of the AC will not only be due to the higher alkali concentration, but even due to the more extended exposure to oxygen during the process of agitation.

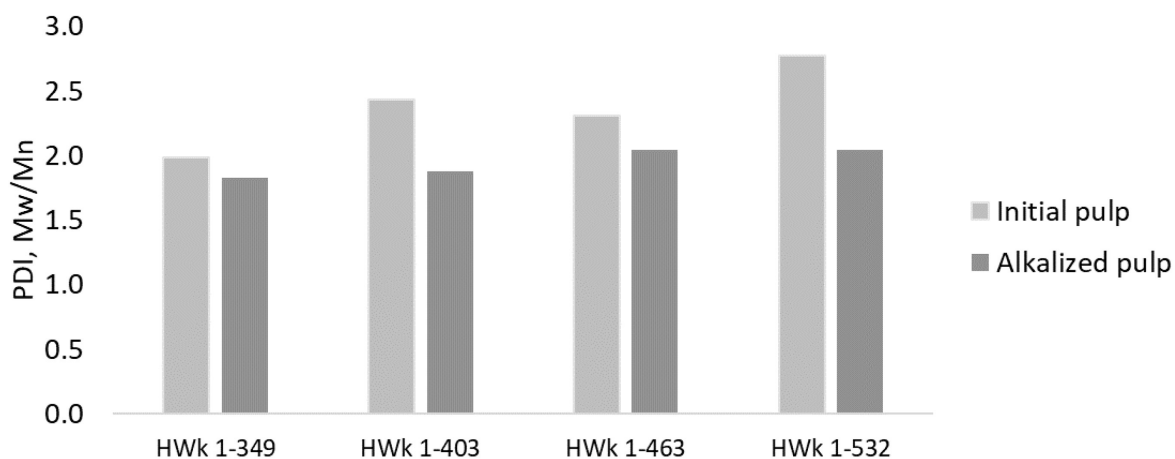
#### 4.2.2 Treatment of pulps with different initial intrinsic viscosity

Within the scope of the supervised master thesis “Aging model of a dissolving market pulp” (Eklund 2021), a series of hardwood kraft dissolving pulp *HWk 1* with different initial intrinsic viscosities from 280 to 530 ml/g was investigated to determine the decrease of intrinsic viscosity due to alkalization. The two pulps with the lowest intrinsic viscosity contained 31-33 mg/g xylan, the pulps with a viscosity of >400 ml/g contained 38 mg/g xylan. It is important to note that these samples were carefully selected from one full-scale production line during a short period of time with the aim of finding clear relationships, and accordingly to give valuable input on the possibility to optimize the alkalization process. Arbitrary selected samples during a long period of time would be less likely to show clear trends as many other occasions within the complex process of pulp production might erase expected trends. The decrease in intrinsic viscosity due to alkalization is important when predicting the course of preaging of specific pulps (2.3). The selected pulps were alkalized with 18 wt% aq. NaOH at 50 °C. It could be shown that intrinsic viscosity after alkalization was in all cases lower than in the initial pulp, and that the difference increased the higher the initial intrinsic viscosity was (Figure 19). Alkalization led in all

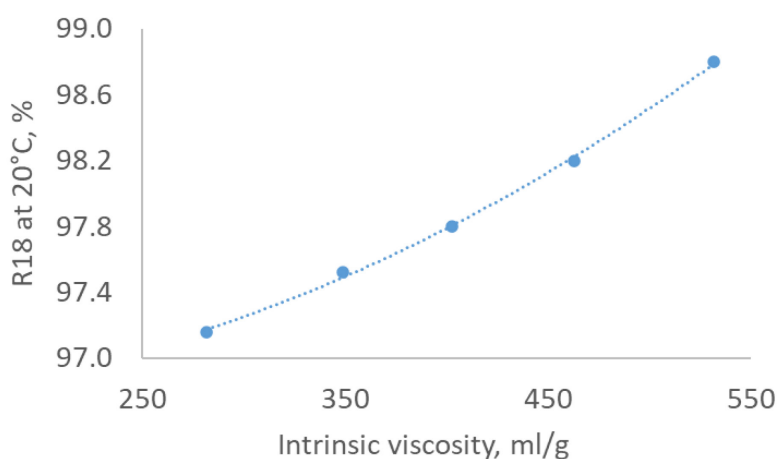


**Figure 19: Intrinsic viscosity of a hardwood kraft dissolving pulp before and after alkalization with 18 wt% aq. NaOH at 50 °C (R18/50) (results taken from Eklund 2021). The data points are marked with the relative decrease in intrinsic viscosity due to alkalization.**

cases to a decrease in PDI (Figure 20). Furthermore, PDI tended to rise with increasing viscosity, both of the original and the alkalinized pulps. The R18-value of the initial samples, determined as residue after extraction with 18 wt% aq. NaOH at 20 °C (R18/20), fell with decreasing intrinsic viscosity (Figure 21) and in the graph it can be seen that R18 decreased by 0.7 %-units /100 ml/g.



**Figure 20: Polydispersity index (PDI) of a hardwood kraft dissolving pulp (HWk) before and after alkalization (R18/50) (results taken from Eklund 2021). The suffix indicates the initial intrinsic viscosity of the test series.**



**Figure 21: R18 at 20 C° versus intrinsic viscosity of a hardwood kraft dissolving pulp before alkalization.**

These results illustrate that pulp processing, which leads to lowering intrinsic viscosity and by this a lowering mean degree of polymerization, caused a more homogeneous molecular weight distribution (PDI) and probably a more open

structure. The lower PDI was a consequence of the fact that the absolute difference between possible minimum and maximum molecular weight became smaller when the molecules underwent more cleavages due to more intensive processing. A more open structure is supposed due to the more intense material loss after alkalization (cf. R18/20), making the cellulose structure more available for aqueous alkaline solutions.

#### 4.2.3 Treatment of different pulp products at a wide span of process conditions <sup>1</sup>

This study elaborated possibilities for the optimization of the alkalization step within the viscose process. Generic pulps and their different regenerated alkali cellulose (rAC) were investigated in detail in terms of their chemical composition and structure properties. The steeping settings applied reflected the settings of commonly used methods to describe the quality of DWP (10 and 18 wt% aq. NaOH at 20 °C) and commonly used parameters in the industry (18 wt% aq. NaOH at 35–50 °C).

Three generically different pulps were studied (Table 3). One long-fiber pulp, originating from softwood, was selected: a sulfite pulp (*SWs 1*) that is used in the production of standard viscose staple fibers (VSF). Short-fiber pulps, originating from hardwood, were represented with two kraft pulps (*HWk 3a*, *HWk 1a-ex*) used in VSF production. *HWk 1a-ex* possessed a somewhat elevated xylan content. Different regenerated alkali celluloses (rAC) were obtained using the procedure for the determination of alkali resistance (ISO 699:2015) (3.2.4). The residue (R) obtained using the procedure was considered as rAC.

##### 4.2.3.1 Change in chemical composition of wood pulp caused by alkalization

The pulps investigated contained different amounts of hemicellulose (Table 3). The lowest mannan content was found in the short-fiber pulps *HWk 3a* and *HWk 1a-ex*. These pulps had two different higher levels of xylan. The long-fiber pulp possessed a high level of mannan. The polydispersity index PDI for the sulfite pulp was found to be significantly higher than that for the kraft pulps, resulting

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<sup>1</sup> This chapter is based on the publication "Influence of pulp characteristics on the properties of alkali cellulose" by C. Fechter, S. Fischer, F. Reimann, H. Brelid and T. Heinze; published in *Cellulose* (London), 2020-08, Vol.27 (12), p.7227-7241

in a generally low level of R-values for the sulfite pulp. This is according to the results discussed in 4.1.

**Table 3: Properties of the investigated pulps**

<i>Sample</i> <sup>a</sup>		<i>SWs 1</i>	<i>HWk 3a</i>	<i>HWk 1a-ex</i>
<b>Chemical composition<sup>b</sup></b>				
Glucan	mg/g	960	970	954
Xylan	mg/g	14	21	37
Mannan	mg/g	21	2	4
Klason lignin	mg/g	0	0	0
Acid-soluble lignin	mg/g	4	5	4
<b>Molecular structure</b>				
Intrinsic viscosity	ml/g	560	417	391
DPw <sup>c</sup>		1752	1132	1048
PDI <sup>d</sup>		6.4	3.1	2.8
C <sub>a</sub> (Raman <sup>e</sup> )	%	54	52	52
Cell I (Raman)	%	43	47	43
Cell II (Raman)	%	3	1	5
<b>Alkali resistance</b>				
R10/20 <sup>f</sup>	wt%	90.1	93.4	93.4
R18/20	wt%	94.4	96.7	96.9
R18/50	wt%	94.3	96.5	95.3
R18/20 – R18/50	wt%	0.1	0.2	1.6

<sup>a</sup> HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp

<sup>b</sup> Saccharides are reported as pure anhydrous polysaccharides. Ash content is not reported.

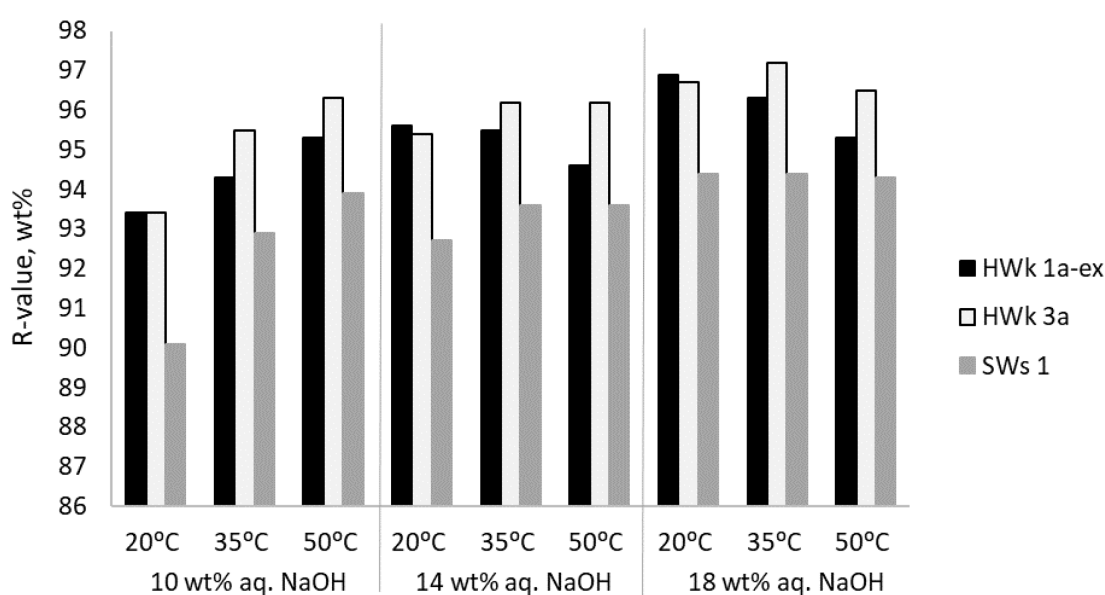
<sup>c</sup> Weight average degree of polymerization determined with GPC-MALS

<sup>d</sup> Polydispersity index determined with GPC-MALS

<sup>e</sup> Parameter of cellulose structure measured with Raman spectroscopy and evaluated according to Agarwal (2017) as a fraction of total cellulose. C<sub>a</sub> – amorphous cellulose, Cell I – cellulose I, Cell II - cellulose II

<sup>f</sup> R – R-value as residue after alkaline extraction, 10 or 18 – wt% aq. NaOH used for extraction, 20 or 50 – extraction temperature in °C

Considering the residue after alkaline treatment, *SWs 1*, *HWk 3a*, and *HWk 1a-ex* showed the same extraction behavior when treated with aq. NaOH (Figure 22). The increasing alkali concentration used for extraction of the pulps (10, 14, and 18 wt% aq. NaOH) resulted in increasing residue levels expressed as R-values when the pulps were extracted at 20 and 35 °C. Lye with an increasing concentration exceeding 10-12 wt% is known to swell the structure of the pulp less (Richter and Glidden 1940), thereby extracting less material from the pulp (Sixta 2006a; Fengel and Wegener 1989).



**Figure 22: Residue, expressed as R-value upon extraction of pulp with aqueous NaOH at different concentrations and temperatures.**

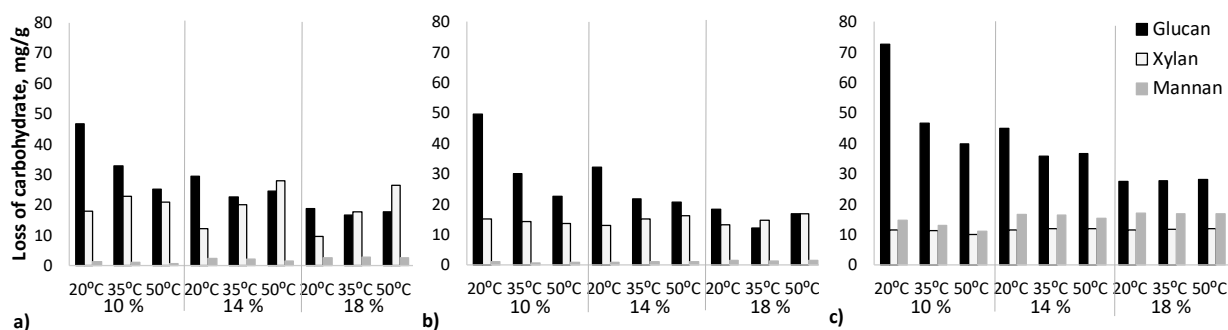
(HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp)

Increasing temperature is known to swell polymeric structures less, too, and increasing temperature counteracts the extraction of material (Sixta 2006a; Fengel and Wegener 1989). Consequently, extraction at 20 °C resulted in a lower R-value than extraction at 35 °C. However, the R-values after alkali extraction at 50 °C cannot be described by the mechanism discussed above. The differences in extracted substance for each pulp became smaller when the aqueous alkali concentration was increased at 50 °C, and all pulps yielded the lowest R-value



after extraction with 14 wt% aq. NaOH. Different properties of SWs 1, HWk 3a, and HWk 1a-ex upon alkali extraction became visible when the influence of temperature on the R-value obtained at different alkali concentrations was analyzed. The R-value when increasing temperature changed from increasing R-value at a low alkali concentration to decreasing R-value at a high alkali concentration. HWk 1a-ex changed already at 14 wt% aq. NaOH to decreasing R-value, HWk 3a at 18 wt%, and SWs 1 remained constant even at the highest alkali concentration applied. SWs 1 showed the absolute maximum of R-value at 18 wt% aq. NaOH at any temperature applied. HWk 3a reached a maximum R-value at 18 wt% and 35 °C, and HWk 1a-ex at 18 wt% and 20 °C.

It was found that less xylan was extracted from *HWk 1a-ex* at 20 and 35 °C when the alkali concentration was increased, which corresponds to the increase in R-value at the same settings (Figure 23). At 50 °C, more xylan was extracted when the alkali concentration was increased to 14 or 18 wt% aq. NaOH. Accordingly, the most xylan was retained after extraction at a high alkali concentration and at a low temperature, the least xylan was retained after extraction at a high alkali



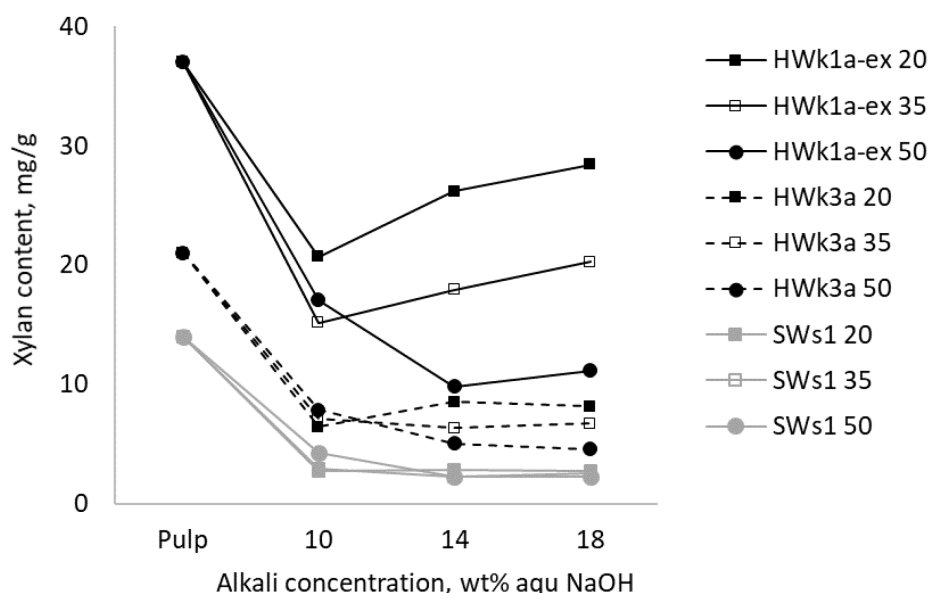
**Figure 23: Loss of carbohydrates in the residue after extraction of pulp with aqueous NaOH at different concentrations and temperatures**

**a) HWk 1a-ex – hardwood kraft pulp with high xylan; b) HWk 3a – hardwood kraft pulp; c) SWs 1 – softwood sulfite pulp**

concentration and a high temperature. *HWk 3a*, which contained less xylan than *HWk 1a-ex*, showed the same behavior but less pronounced. Extracting *SWs 1*, where mannan was the main hemicellulose component, the absolute loss of both xylan and mannan was maximal when using 14 or 18 wt% aq. NaOH alkali concentration at any temperature applied. The extraction behavior for *SWs 1*,

*HWk 3a*, and *HWk 1a-ex* had in common that glucan was the most intensely extracted component at a low temperature and a low concentration of alkali (20 °C and 10 wt% aq. NaOH), xylan was the most intensely extracted at a high temperature and a high concentration of alkali (50 °C and >14 wt% aq. NaOH), and mannan was the most intensely extracted at an alkali concentration >14 wt% aq. NaOH at all temperatures applied.

Sixta and Schrittwieser (2004) have investigated the properties of a beech sulfite pulp upon extraction with aqueous alkali at different temperatures. The key properties of this pulp were found to be equal to the *HWk 1a-ex* of the present study (R18 93.4 %; 4.0 % xylan). Those authors have found that xylan removal has been more efficient at 20 °C than at higher temperatures as the alkali concentration has had to be increased from 100 to 150 g/l to reach the lowest possible xylan content in the pulp at 50 and 80 °C. The present study confirms that extraction maximum at low temperatures (20 and 35 °C) can be expected with 10 wt% aq. NaOH (Figure 24), which highlights that a higher temperature (50 °C) results in even higher levels of xylan extraction when the alkali conen-



**Figure 24: Profiles of xylan content in the regenerated residue of three different pulps after alkaline extraction at different concentrations and temperatures (10, 14 and 18 wt% aq. alkali; 20, 35 and 50 °C)**

**(HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp. 20, 35 resp. 50 – temperature in °C used for alkali extraction)**

tration is increased from 10 to 14 and 18 wt% aq. NaOH. *SWs 1*, *HWk 3a* and *HWk 1a-ex* seemed to have different extraction optima, however, that was not possible to be exactly determined in this study. *HWk 1a-ex*, with the highest initial xylan content, illustrated the process of xylan removal upon alkalization within the investigated settings in accordance with Sixta and Schrittwieser; the lower the extraction temperature, the lower the alkali concentration needed to reach a maximum in xylan extraction from pulp. *HWk 3a* and *SWs 1* with lower initial contents of xylan are assumed to develop in the same way, but to a less pronounced extent.

#### 4.2.3.2 The change in carbohydrate structure caused by alkalization

##### **Molecular weight**

After alkaline extraction, all pulps obtained a decreased amount of material with DP <50 and <100, as this fraction was removed in the form of hemicellulose and low molecular-mass cellulose (Table 4 and Figure 23). Furthermore, a slight chemical degradation of the carbohydrates at 50 °C could be expected according to data in the literature (Mozdyniewicz et al. 2013, Sixta et al. 2004 and Sixta 2006a). The data of this study showed no clear difference in polymer degradation due to temperature or alkali concentration. The relative increase in the fraction of DP >2000 for all pulps was, instead, a consequence of the decrease in the fraction of low-molecular-weight substance after extraction (Table 4). The corresponding distribution of molecular weight shown in the appendix (Figure 55) illustrates how the material of high molecular weight was successively degraded to a lower molecular weight, which led to a decrease in Mw. This successive degradation was less pronounced for the short fiber kraft pulps. Kraft pulps had a lower PDI than the sulfite pulps, which resulted in less material to be degraded and extracted. A degradation of intercrystalline-available low molecular-weight hemicelluloses could not be followed in this study, as those degraded molecules had left the sample upon pressing. This possible degradation could explain the increased extraction of xylan from pulp at high alkali concentrations and temperatures. The extraction with 10 wt% aq. NaOH at 20 °C (10/20) counted for the highest decrease in low-molecular-

weight substances and can most likely be related to the large decrease in glucan at low alkali concentrations and temperatures (Figure 23).

**Table 4: Molecular-weight-related properties of pulps and their alkali extracts determined with size-exclusion chromatography. Molecular weight distributions are shown in the appendix (Figure 55).**

Sample <sup>a</sup>	$M_w$ , kg/mol	PDI <sup>b</sup>	DP <sup>c</sup> <50, %	DP <100, %	DP >2000, %
SWs 1	284	6.4	3.2	7.3	25.8
SWs 1 10/20	246	3.2	0.2	1.1	30.0
SWs 1 10/50	248	3.6	0.4	1.9	29.9
SWs 1 18/20	238	3.9	0.7	2.6	29.4
SWs 1 18/50	213	3.5	0.6	2.6	26.3
HWk 3a	183	3.1	1.8	4.7	13.3
HWk 3a 10/20	168	2.3	<0.1	0.6	17.3
HWk 3a 10/50	153	2.7	0.6	2.3	15.3
HWk 3a 18/20	165	2.7	0.4	1.9	17.8
HWk 3a 18/50	158	2.4	0.1	1.3	16.1
HWk 1a-ex	155	2.8	1.1	3.9	12.4
HWk 1a-ex 10/20	165	2.7	0.3	1.8	16.9
HWk 1a-ex 10/50	158	2.6	0.3	1.7	15.6
HWk 1a-ex 18/20	156	2.8	0.4	2.6	15.8
HWk 1a-ex 18/50	151	2.7	0.5	2.3	14.6

<sup>a</sup> HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp, xx/yy – 10 or 18 wt% aq. NaOH, 20 or 50 °C used for extraction

<sup>b</sup> Polydispersity index ( $M_w/M_n$ )

<sup>c</sup> Degree of polymerization

The extraction of substance of low-molecular mass is supposed to decrease PDI. This became obvious for *SWs 1*, in which PDI decreased from 6.4 in the raw material to below 4.0 in the extracted samples. PDI in *HWk 3a* decreased, to a lesser extent, from 3.1 to significantly below 3.0. The minor decrease in PDI of *HWk 1a-ex*, which had a low initial PDI of 2.8, highlights that the extracted substance (3.1 - 6.6 wt% according to the determined R-values, Figure 22) had a

molecular weight distribution that extended into the high molecular weight fraction. No further general explanations for the differences between the different extraction settings in the investigated pulps could be found.

### Transformation of cellulose I to cellulose II

The transformation of cellulose I (Cell I) to Cell II upon the regeneration of alkalized pulp (rAC) is a measure of the transformation of Cell I to sodium cellulose by alkalization and, consequently, a measure of the reactivity of the pulp. Röder et al. (2006) have reported FT-Raman to be a fast and precise method in comparison to wide-angle X-ray scattering (WAXS), which is the standard method for determining the crystallinity of Cell II. Schenzel et al. (2009) and Agarwal (2017) have proposed different approaches using Raman spectroscopy for the determination of Cell II in the crystalline part of a sample. Schenzel et al. have used the ratio of the intensities I at 1477 cm<sup>-1</sup> to 1464 cm<sup>-1</sup> and at 379 cm<sup>-1</sup> to 352 cm<sup>-1</sup>, Figure 25. Agarwal (2017) has used the ratio 577 cm<sup>-1</sup> to 1096 cm<sup>-1</sup>. Even though Agarwal's approach is dedicated to characterizing nanofibrillated cellulose, these three approaches correlated well to each other when the data obtained in the present study were used. The approach given by Agarwal (Equation 5) was chosen for this evaluation. The change of intensity at 577 cm<sup>-1</sup>, which clearly illustrates the structural change of the cellulose when applying the different alkalization settings in the present study, is shown in the appendix (Figure 56). The evaluation was complemented with the approach for amorphous cellulose C<sub>a</sub> from the same reference (Equation 6), and the completion to 100 % was interpreted as the proportion of Cell I (Equation 7). This value for Cell I was, on average, 8% units lower than the Raman crystallinity index X<sub>CRaman</sub> established by Schenzel et al. (2005) (Cell I = 1.0422 X<sub>CRaman</sub> - 8.032. R<sup>2</sup> = 0.9841). The approach by Schenzel et al. (2005) uses the ratio of the intensities at 1481 cm<sup>-1</sup> and 1462 cm<sup>-1</sup> as an expression for the degree of crystallinity of partially crystalline Cell I samples.

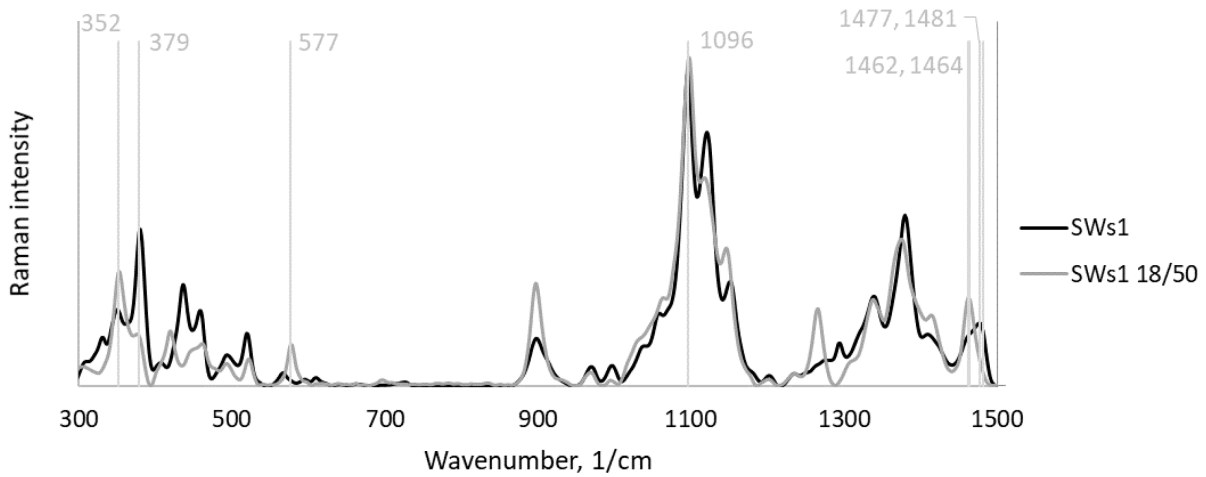
$$\text{Cell II [\% of crystalline share]} = \frac{\frac{I_{577} - 0.009}{I_{1096}}}{0.0013} \quad \text{Equation 5}$$

$$C_a [\% of total cellulose] = \frac{I_{1380}}{I_{1096}} \times 100 \quad \text{Equation 6}$$

$$\text{Cell I [\% of total cellulose]} = (100 - C_a) \times \frac{100 - \text{Cell II}}{100} \quad \text{Equation 7}$$

The degree of transformation ( $D_T$ ) of the pulp into sodium cellulose was calculated as an increase in Cell II upon alkalization and regeneration (Equation 8).

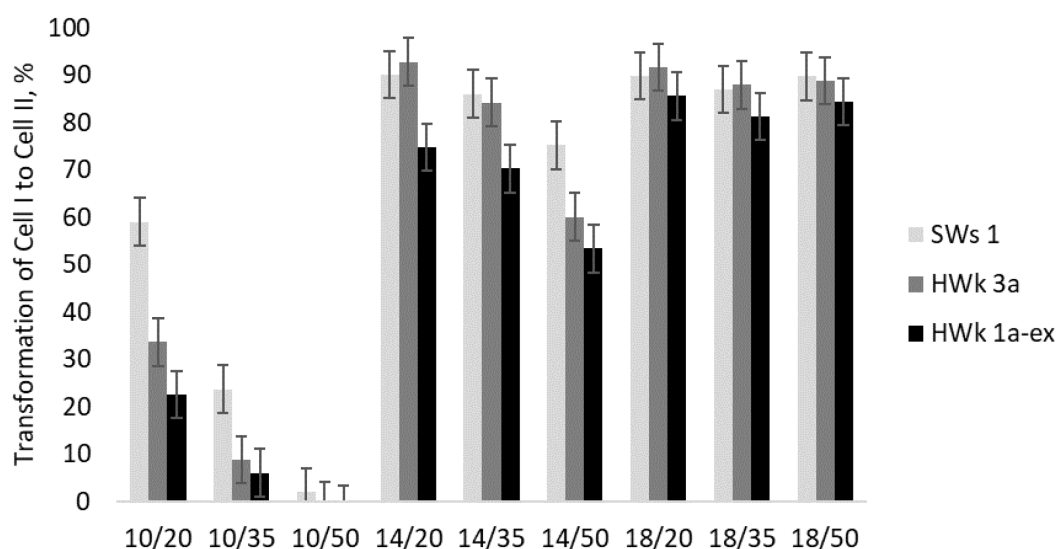
$$D_T = \frac{100 \times (\text{Cell II}_{rAC} - \text{Cell II}_{DWP})}{100 - \text{Cell II}_{DWP}} \quad \text{Equation 8}$$



**Figure 25: Raman spectra of the softwood sulfite pulp (SWs 1) in native form and after alkaline extraction with 18 wt% aq. NaOH at 50 °C (SWs 1 18/50). Bands of interest for evaluation of cellulose structure are marked.**

According to the literature, alkali concentrations of  $\geq 16$  wt% aq. NaOH at 20 °C lead to the complete transformation of Cell I to Cell II upon regeneration (Sisson and Saner 1941, Fink et al. 1982). The highest  $D_T$  achieved in this study was only 93 % (Figure 26). This points to the relative character of Raman spectroscopy and the need for the calibration of specific series when using this technique. The relative difference between the investigated settings and the different pulps can be evaluated well, despite this issue. The transformation of Cell I to Cell II increased with increasing alkali concentration and decreasing temperature. This result is in line with findings by Sisson and Saner (1941) and Reyes et al. (2016). A clear ranking of the severity of the increase in alkalization in terms of conformation transformation was given by concentration ( $10 < 14 < 18$  wt% aq. NaOH). A ranking by temperature was less pronounced and most obvious at

10 and 14 wt% aq. NaOH ( $50 < 35 < 20$  °C). A transformation at 10/50 was hardly recognizable for any of the pulps and was found to be the weakest treatment followed by 10/35, 10/20 and 14/50. At these treatments, *SWs 1* was distinguished as the most reactive pulp. This finding is in accordance with the observations of Sixta and Borgards (1999), where acid sulfite pulps have been found to require a lower lye concentration for the lattice transformation to Na-Cell than kraft pulps. At harsher conditions (14/35 and 14/20), *HWk 3a* reached the same level as *SWs 1*. These pulps showed a tendency toward a higher proportion of  $C_a$  or a lower proportion of Cell II (Table 3), which might contribute to an easier transformation. At 18 wt% aq. NaOH, temperature had less influence on this transformation, and only minor differences in reactivity among the investigated pulps could be seen. For *SWs 1* and *HWk 3a*, a maximum of transformation was achieved using 14 wt% aq. NaOH at 20 °C. *HWk 1a-ex* reached that transformation level at 18 wt% aq. NaOH. The earlier and more pronounced transformation of *SWs 1* and *HWk 3a* can be related to the highest degree of  $C_a$  (*SWs 1*) and the lowest degree of Cell II (*HWk 3a*) (cf. Table 3), which are supposed to favor the reactivity of a pulp.



**Figure 26:** Transformation of Cell I to Cell II of different pulps (*HWk 1a-ex* – hardwood kraft pulp with high xylan, *HWk 3a* – hardwood kraft pulp, *SWs 1* – softwood sulfite pulp) upon alkalization at different concentrations and temperatures; concentration of aqueous NaOH: 10, 14 or 18 wt%; temperature 20, 30, or 50 °C. The accuracy of the measurement is assumed to  $\pm 5$  %-units.

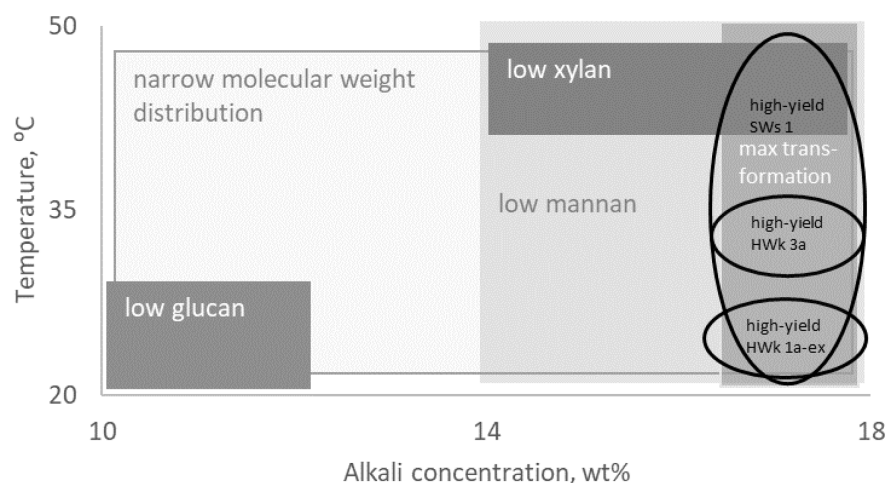
#### 4.2.3.3 Optimizing the alkalization step

This study identified differences and similarities between conventional dissolving wood pulp (DWP) as summarized in Figure 27 and, thus, room for process optimization in the process step of steeping with alkali. The long-fiber sulfite pulp (*SWs 1*) with an initially low content of xylan and high PDI reached the highest purity from hemicelluloses (7 – 8 mg/g, cf. Table 3 and Figure 23c) when it was extracted with 14 or 18 wt% aq. NaOH. For this pulp, the yield, determined as R-value, varied from 90.1 to 94.4 % with the conditions applied (Figure 22). This large variation emphasizes the need for optimizing steeping conditions in order to minimize loss in yield. A maximum yield of >94 % was reached using 18 wt% aq. NaOH. The R-value was not affected by temperature at this alkali concentration. The short-fiber kraft pulps with low PDI and low and high initial content of xylan (*HWk 3a* and *HWk 1a-ex*, respectively) reached the highest purity from hemicelluloses with 14 or 18 wt% aq. NaOH at 50 °C (5 - 6 resp. 12 – 13 mg/g, cf. Table 3 and Figure 23a and b). Residual xylan in *HWk 1a-ex* varied between 12 and 30 mg/g over the entire investigated range of conditions, which underlines the importance of optimizing this property when steeping. A maximum yield of >96 % for both short-fiber kraft pulps was reached using 18 wt% aq. NaOH at 20 or 35 °C (*HWk 1a-ex* resp. *HWK 3a*). Molecular weight distribution was not critical when steeping the three pulps. All settings produced a regenerated AC (rAC) with decreased or low PDI. The maximum transformation of *SWs 1* and *HWk 3a* to Cell II via Na-Cell occurred already with 14 wt% aq. NaOH at 20 and 35 °C. *HWk 1a-ex* needed 18 wt% aq. NaOH for the maximum transformation. *SWs 1* stood out as the pulp most robust for steeping conditions. High purity and a transformation to Na-Cell were achieved with 14 wt% aq. NaOH at 20 or 35 °C. For the sake of yield optimization, a higher alkali concentration at a temperature between 20 and 50 °C would be preferable. Steeping *HWk*, and especially *HWk 1a-ex*, with 18 wt% aq. NaOH at different temperatures would compromise either yield or purity while the transformation to Na-Cell would be at the maximum. Extracting 3 mg/g or 0.3 % more xylan from *HWk 3a* while increasing the temperature from 35 to 50 °C decreased yield by 0.7 %-units, which is 0.4 % additional yield loss caused by the extraction of other carbohydrates. Yield should be optimized using a temperature <50 °C. *HWk 1a-ex* behaved similarly, but on a higher



absolute level of property changes, which makes optimization of the settings more important. High alkali (18 wt% aq. NaOH) is necessary for the maximum transformation to Na-Cell. Extracting 17 mg/g or 1.7 % more xylan while increasing the temperature from 20 to 50 °C decreased the yield by 1.6 %-units, which means no further yield loss caused by the extraction of other carbohydrates. Purity should be optimized using a temperature >20 °C.

An illustration of the yield-purification relationship among the different investigated pulps based on the discussed data is shown in the appendix (Figure 57).



**Figure 27: Similarities and differences of three different dissolving wood pulps (HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp ) upon alkaline extraction**

#### 4.2.4 Treatment of a selected pulp product at a specific span of process conditions <sup>2</sup>

Regarding the optimal steeping concentration, the results presented in 4.2.3 complied with former studies from Wyatt (1966), Reyes et al. (2016) and the observation from Woodings (2001). All pointed to high concentration to favor the process of steeping dissolving pulp. High concentration corresponded to 17-

<sup>2</sup> This chapter is based on the publication “Possibilities for Optimization of Industrial Alkaline Steeping of Wood-Based Cellulose Fibers” by C. Fechter, S. Fischer and H. Brelid; published in *Molecules* (Basel, Switzerland), 2020-12-10, Vol.25 (24), p.5834

21 wt% aq. NaOH. In 4.2.3 it could be noted that the high alkali concentration led to the best alkalization result for yield, purity from xylan, and transformation (Figure 27).

Regarding the optimal steeping temperature, the studies from Wyatt (1966) and Reyes et al. (2016) and the observation from Woodings (2011) did not point to a common temperature span which could favor the process of steeping dissolving pulp. The study presented in 4.2.3 could however clarify that the choice of steeping temperature became important with increasing xylan content of the dissolving pulp. The lower range of extraction temperature – corresponding to 15 and 29 °C as proposed by Wyatt (1966) and Reyes et al. (2016), respectively - favored yield, but led to lower purity from xylan. Consequently, the importance of process optimization in the alkalization step could be identified when using xylan-rich dissolving pulps.

The study presented in this chapter investigated a market pulp (*HWk 2a*) similar to the xylan-rich pulp investigated in 4.2.3 (*HWk 1a-ex*) applying a narrower range of steeping settings that mirrors today's viscose production conditions (17-20 wt% aq. NaOH at 40-50 °C) similar to those observed by Woodings (2001). Based on the findings in 4.2.3 and using the same methodology and facilities, the aim of this study is to show whether the narrow span of commonly applied settings has the potential for further process optimization regarding the purity, the yield, and the degree of transformation to sodium cellulose (Na-Cell) in the alkalization step.

*HWk 2a*, a hardwood kraft dissolving pulp for use in viscose fiber production, was characterized as summarized in Table 5. The fact that the process history and the chemical composition of *HWk 2a* was almost identical to *HWk 1a-ex*, made it possible to further develop the research conducted in 4.2.3. However, the molecular weight of *HWk 2a* deviated from *HWK 1a-ex* with regard to higher molecular weight (474 ml/g vs. 391 ml/g) and broader molecular weight distribution (higher polymer dispersion index, PDI; 3.3 vs. 2.8). In consequence, *HWk 2a* had a lower fraction of low molecular weight material (DP < 100) and a higher fraction of high molecular weight material (DP > 2000). Nevertheless, both pulps were still in the normal range of a standard kraft dissolving pulp. The present study investigated the two independent variables alkali

concentration [NaOH] and extraction temperature T. All experimental data are given in Table 5.

**Table 5: Properties of the hardwood kraft dissolving pulp HWk 2a (-) investigated and experimental data for the residues after alkaline extraction at different alkali concentrations of aqueous NaOH and temperatures**

NaOH- conc.	wt%	-	17	17	18	18	18	18	19	19	20	20
Extraction temp.	°C	-	40	44	40	42	44	50	42	44	40	50
Residue <sup>a</sup>	wt%	-	96.1	95.8	96.5	96.2	96.0	95.5	96.2	96.1	96.6	95.6
Glucan <sup>b</sup>	mg/g	953	978	980	976	977	979	983	978	978	976	982
Xylan <sup>b</sup>	mg/g	39	17	14	18	17	15	11	17	16	18	13
Mannan <sup>b</sup>	mg/g	4	2	2	2	2	2	2	2	2	2	2
Mn	kg/mol	65	57	49	72	71	61	65	68	71	66	46
Mw	kg/mol	215	182	166	178	189	187	185	183	189	179	158
Mz	kg/mol	466	371	355	332	374	367	355	353	369	334	322
PDI <sup>c</sup>		3.3	3.2	3.4	2.5	2.7	3.1	2.8	2.7	2.7	2.7	3.4
DP <sup>d</sup>		1327	1123	1025	1099	1169	1153	1141	1130	1167	1107	975
DP<50	%	0.9	1.0	1.6	0.2	0.4	1.0	0.7	0.4	0.4	0.5	1.4
DP<100	%	2.8	2.7	3.7	1.2	1.6	2.5	2.0	1.6	1.6	1.8	3.6
DP>2000	%	18.6	14.7	12.7	13.5	14.8	15.3	14.6	14.3	14.9	13.9	11.7
D <sub>T</sub> <sup>e</sup>	%	-	86	88	88	85	87	86	85	86	88	85

<sup>a</sup> All settings despite of the extraction with 18 wt% aq. NaOH at 42 °C were repeatedly determined. The real pooled difference for the residues after alkaline extraction in this study is 0.08 %-units, to compare with 0.3 %-units given in the standard procedure.

<sup>b</sup> The saccharides are reported as pure anhydrous polysaccharides

<sup>c</sup> Polydispersity index, determined with GPC-MALS

<sup>d</sup> Weight average degree of polymerization, determined with GPC-MALS

<sup>e</sup> Degree of Transformation measured with Raman spectroscopy and evaluated according to Equation 8 as a fraction of crystalline cellulose

A multiple linear fitting of the data for the response variables residue after alkaline extraction (R-value) and the xylan content in the residue was possible according to Equation 9 and 10. The correlation coefficient  $R^2$  and- the estimate of the predictive ability of the model  $Q^2$  were both high and close to each other

for both responses, R-value (0.95 and 0.87, respectively) and xylan content (0.98 and 0.93, respectively). All other measured responses (data from molecular weight distribution and degree of transformation) had  $R^2 < 0,4$  and a negative  $Q^2$ , which show that no statistically firm modelling could be done.

$$R - value = 91.423 + 0.464 [NaOH] + 0.056 T - 0.008 ([NaOH] \times T)$$

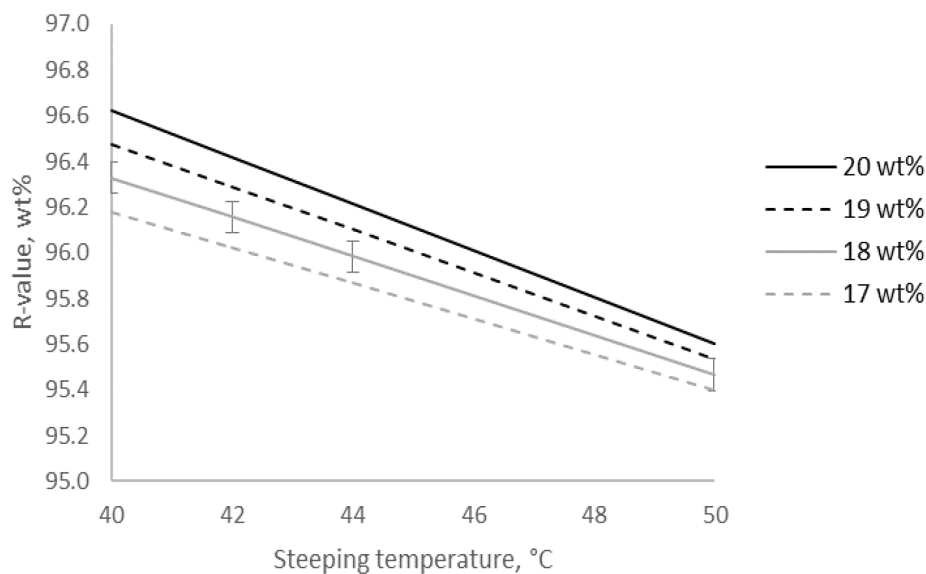
Equation 9

$$Xylan\ content = 43.355 + 0.002 [NaOH] - 0.874 T + 0.013([NaOH] \times T)$$

Equation 10

#### 4.2.4.1 The change in yield of the pulp caused by alkalization

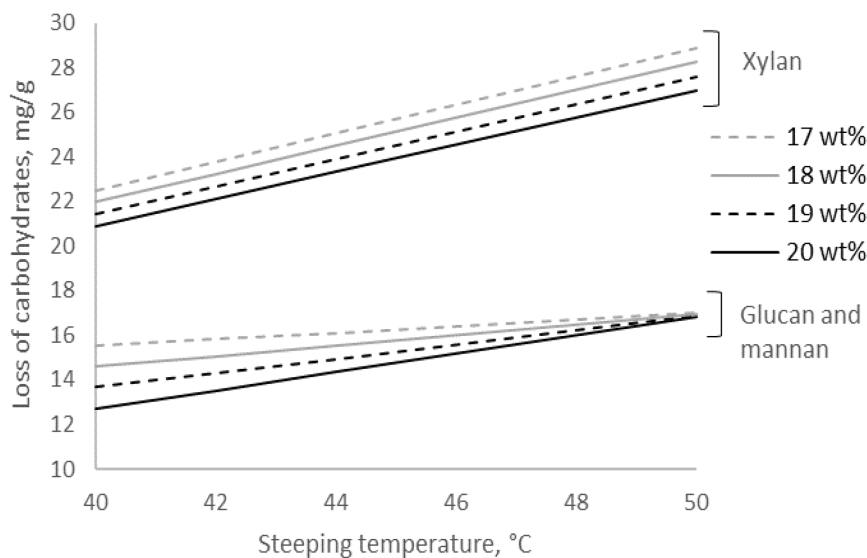
It is shown in literature that yield after alkaline extraction increases with increasing alkali concentration exceeding 10-12 wt% aq. NaOH and increasing temperature as these conditions lead to a less swollen structure hampering the extraction of polymeric material and leading to higher R-values (Fengel and Wegener 1989, Sixta 2006a, Richter and Glidden 1940). This study quantified the increase of R-value due to increased alkali concentration to 0.2 - 0.4 %-units depending on extraction temperature when increasing from 17 to 20 wt% aq. NaOH, Figure 28. The R-value decreased 0.8 - 1.0 %-units when increasing temperature from 40 to 50 °C. This result was contradictory to general understanding, but in accordance with the results presented in 4.2.3. There it was shown for three basically different dissolving pulps that increasing temperature has led to lower R-value at alkali concentrations  $\geq 14$  wt% aq. NaOH. This trend was even more pronounced for the pulp with the highest xylan content (*SWk 1a-ex*). The xylan rich hardwood kraft dissolving pulp was comparable to the pulp used in this study.



**Figure 28: Modelled residue after extraction of hardwood kraft dissolving pulp HWk 2a with aqueous NaOH at different concentrations and temperatures, expressed as R-value, and its RMSE.**

#### 4.2.4.2 The change in purity of the pulp caused by alkalization

Chapter 4.2.3., where a wide span and a low resolution of extraction settings (10, 14, and 18 wt% aq. NaOH at 20, 35, and 50 °C) was studied, showed the highest purity regarding xylan at relatively less loss of glucan, i.e. the highest selectivity, to be reached after extraction with high alkali concentration at high temperature (18 wt% aq. NaOH at 50 °C). The present study investigated these extraction settings in more detail and confirmed the finding that purification from xylan was most intense at 50 °C, which again was the highest temperature of the investigated span (Figure 29). The modelled data revealed a tendency for the highest selectivity for extraction of xylan to be at the lowest investigated alkali concentration (17 wt% aq. NaOH) at 50 °C. At 50 °C, same amounts of glucan and mannan were modelled to be extracted independent on the alkali concentration applied.

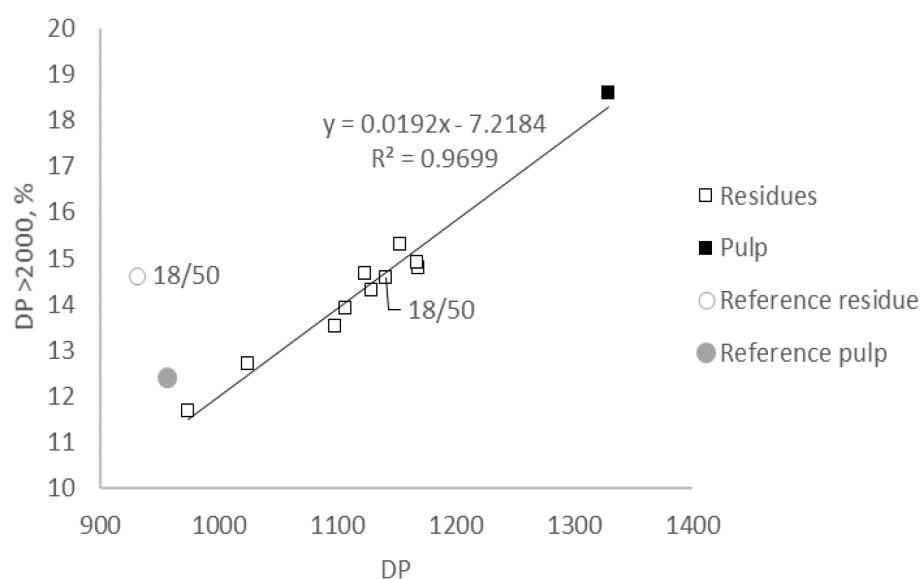


**Figure 29: Modelled loss of carbohydrates in the residue after extraction of pulp with aqueous NaOH at different concentrations and temperatures.**

#### 4.2.4.3 Molecular weight

The results obtained from GPC-MALS allowed no statistically firm modelling of the influence of the factors alkali concentration and temperature for the extractions done with 17-20 wt% aq. NaOH at 40-50 °C (Table 5). Interestingly, both the fraction of DP > 2000 and the Mw or DP decreased for all alkaline extraction settings applied. The decreases were found to be linearly positive correlated with  $R^2 = 0.97$  (Figure 30). These results were in contrast with the findings presented in 4.2.3. In that study, the investigated pulp *HWk 1a-ex*, which differed from the investigated pulp in the present study by a lower DP, increased in fraction of high molecular weight material, while DP decreased slightly for the whole span of extraction settings applied (10-18 wt% aq. NaOH at 10-50 °C). The low-molecular weight fraction decreased at the same time. The resulting polydispersity index (PDI) was almost stable with a tendency for decrease. In the present study, no general trend for these expected trends upon alkaline extraction, i.e. purification from low molecular material and decrease of the PDI could be observed. This fact can be explained with the higher molecular weight of the sample in the present study. For a pulp with a low initial intrinsic viscosity, the purification from short molecular weight material will dominate the molecular structure after alkaline extraction (less low

molecular weight material results in a larger fraction of high molecular weight and smaller PDI). For the actual pulp with a ca. 80 ml/g higher intrinsic viscosity the deterioration of the high molecular weight dominated the molecular structure after alkaline extraction with a smaller fraction of high molecular weight material in the residues. The trend for low molecular weight material and PDI was indifferent. The most extraction settings led to a reduction of low-molecular weight fractions and the PDI. However, extraction with 17 wt% aq. NaOH at 44 °C and 20 wt% aq. NaOH at 50 °C led to an increase in both low molecular weight fraction and PDI compared to the properties in the initial pulp sample. No explanation was found for these results, but it can be concluded that the higher alkali concentration ( $\geq 18$  wt% aq. NaOH) in combination with the lower temperature span ( $\leq 44$  °C) resulted in the highest decrease of PDI.



**Figure 30: Correlation of degree of polymerization (DP) and fraction of material with DP > 2000 as determined with GPC-MALS after alkaline extraction of hardwood kraft dissolving pulp HWk 2a with 17-20 wt% aq. NaOH at 40-50 °C. The reference pulp is HWk 1a-ex with lower viscosity but identical chemical composition) and its residue after extraction with 18 wt% aq. NaOH at 50 °C.**

#### 4.2.4.4 Transformation of cellulose I to cellulose II

The degree of transformation to sodium cellulose (Na-Cell) can be determined by the analysis of the content of cellulose II (Cell II) before and after alkalization

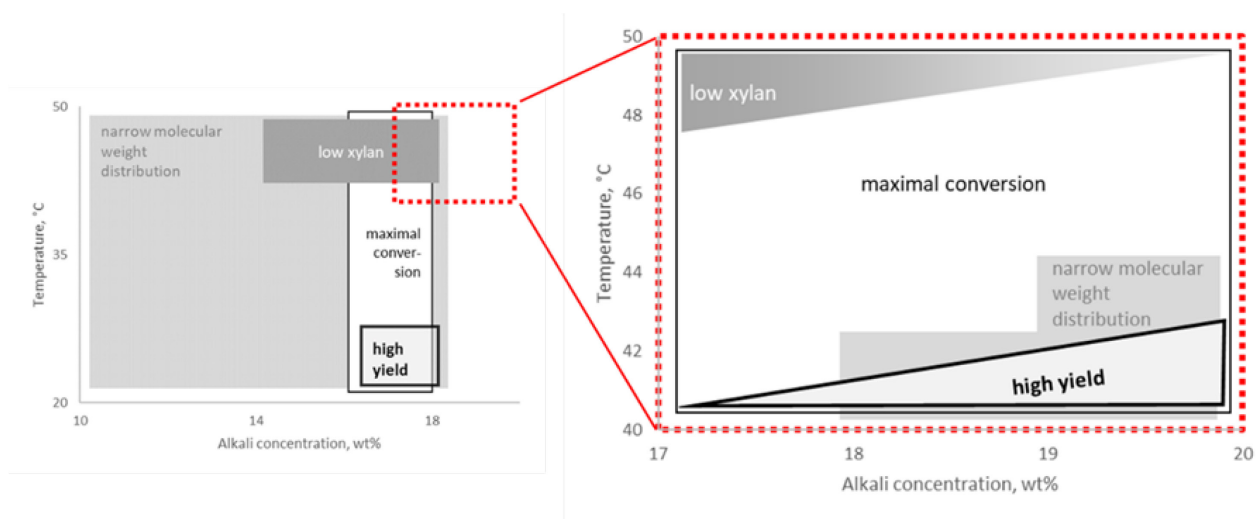
and regeneration. This is because native cellulose exists as the specific lattice cellulose I (Cell I). This lattice is still the main fraction of the crystalline fraction in the pulp investigated (Table 5). When washing and neutralizing the alkalinized pulp, and thus removing NaOH from Na-Cell, regeneration into the thermodynamically more stable crystal lattice of Cell II takes place (Sisson and Saner, 1941; Okano and Sarko, 1985). The degree of transformation gives information on the resistance of a specific pulp to alkalization. The accuracy of the determination of the degree of transformation with Raman-spectroscopy as introduced in 4.2.3. was assumed to 5 % and no differences between the extractions done with 17-20 wt% aq. NaOH at 40-50 °C could be stated in the present study. The alkaline treatments led to a degree of transformation of ca. 86 % as the 95 % confidence interval for the mean conversion of all samples was  $86.3 \pm 2.5$  %. This degree of transformation corresponded to the transformation for that kind of pulp under comparable conditions reported in 4.2.3..

#### 4.2.4.5 Optimizing the alkalization step

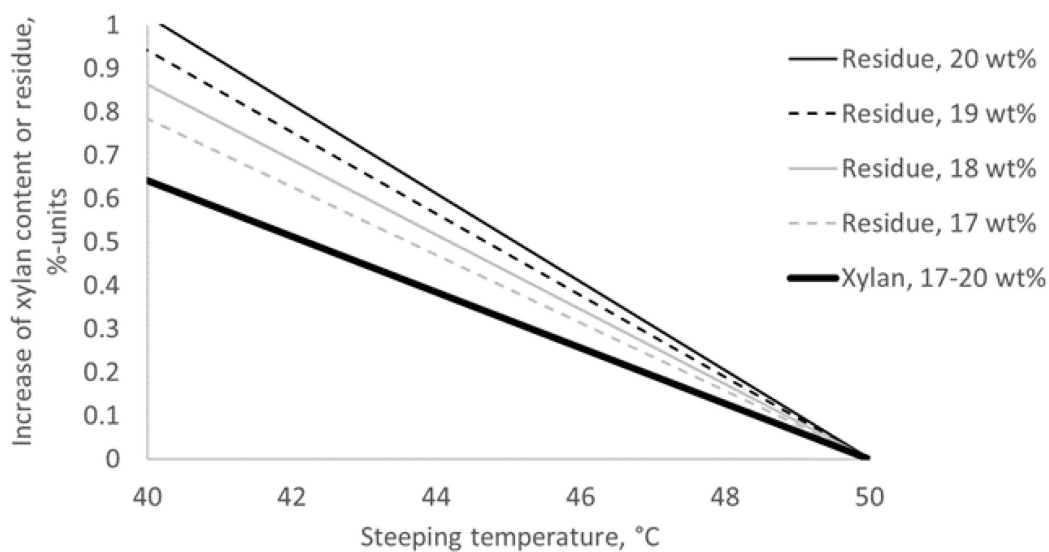
This study gave both reliable and logical results when investigating the narrow range of alkalization settings used in industrial processes (17-20 wt% aq. NaOH at 40-50 °C). The trends shown for the settings when optimizing towards low xylan, high yield, and maximal conversion to sodium cellulose (Na-Cell) both complement and develop the findings in 4.2.3. (Figure 31). Low xylan content and high yield could be shown to be contradicting within the applied narrow range of extraction settings with primarily low temperature and secondly high alkali concentration favoring yield. They varied to an extent that makes case-adapted process optimization meaningful.

Best selectivity was found after extraction with low alkali concentration at the high temperature of 50 °C. At the same time, yield was on a minimum within the investigated range of extraction settings. A decrease of the steeping temperature by 2 °C when extracting with 17 wt% aq. NaOH would increase yield with 0.15 %-units, extracting with 20 wt% would lead to an increase of 0.20 %-units (Figure 32). When optimizing for higher yield by extracting at lower temperature, higher alkali concentration would even result in a lower xylan content in the residue at a given yield as residue (Figure 33).

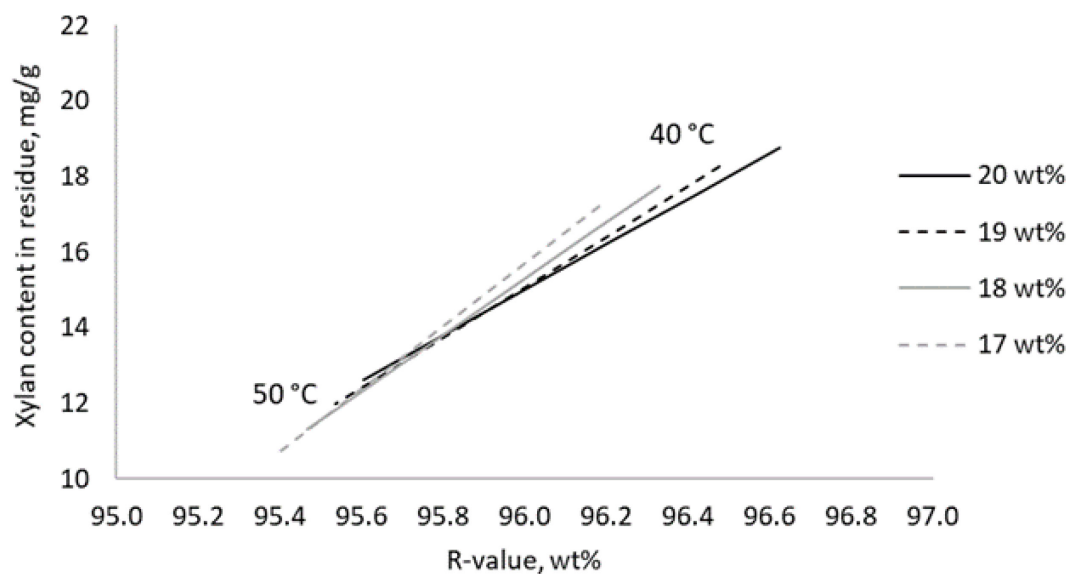




**Figure 31: Trends for the key parameters yield, xylan content, conversion to alkali cellulose and molecular weight distribution for different alkaline extraction settings of dissolving pulp. The illustration of the wide span of settings to the left is as presented in 4.2.3, Figure 27.**



**Figure 32: Change in xylan content and residue after extraction of hardwood kraft dissolving pulp with 17-20 wt% aq. NaOH when decreasing the steeping temperature from 50 to 40 °C.**



**Figure 33: Modelled correlation between residue after extraction of hardwood kraft dissolving pulp with aqueous NaOH at different concentrations and temperatures, expressed as R-value, and the xylan content left in its residue.**

The finding that the yield favoring conditions higher alkali concentration and lower extraction temperature resulted in a narrower molecular weight distribution (lower PDI) for the specific pulp investigated was unexpected. In any case, the hypothesis that alkaline extraction parameters matter for the resulting distribution of different molecular weight fractions could be neither refused nor confirmed. For further research work it is assumed that the initial molecular weight and its distribution in the pulp might play an important role for the resulting distribution of molecular weight fractions in the residue. Consequently, it would be of interest to further investigate how the initial molecular weight in a pulp influences the distribution of different fractions after alkaline extraction.

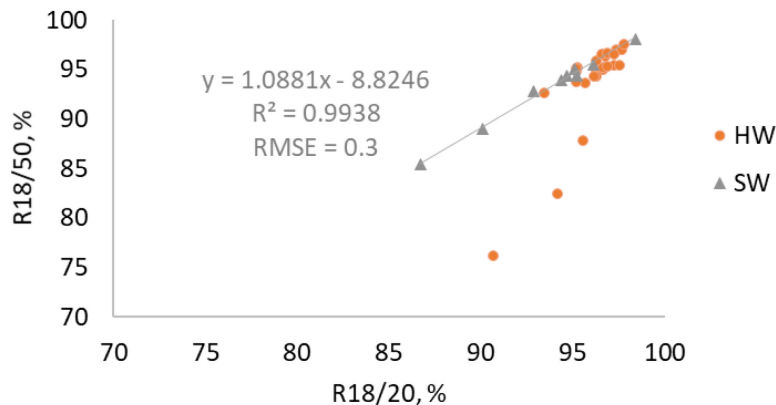
#### 4.2.5 Predicting alkalization yield at full-scale conditions

Standard extraction settings determining the pulp residues R18 and R10 (here R18/20 and R10/20) are 18 and 10 wt% aq. NaOH at 20 °C, respectively. These two properties are used to estimate the pulps cellulose content and the yield after alkalization. As industrial alkalization is frequently done at 45 – 55 °C

(Woodings 2001), an additional analysis of R18 at 50 °C (R18/50) would be useful to estimate the real yield after alkalization. Some 34 of the previously-discussed pulps deliver complete data sets for R18/20 and R18/50 and many other properties (Appendix, Table 14). These pulps cover a wide range of commercially-available dissolving wood pulps from both hard- and softwood, as well as paper pulps and specific lab samples. A higher amount of extracted material from the pulp and consequently a lower R-value due to extraction at a higher temperature and a high alkali concentration (R18/50) was confirmed in all 34 cases. The lowest empirical decrease found was 0.1 %-units, the highest decrease found for dissolving wood pulp (DWP) was 2.2 %-units and the maximal decrease was found to be 14.6 %-units for a hardwood kraft paper pulp (HWk-paper).

For softwood pulps, R18/50 correlated linearly to R18/20 (Figure 34 and equation 11):

$$R18/50_{SW} = 1.0881 \times R18/20_{SW} - 8.8246 \quad \text{Equation 11}$$



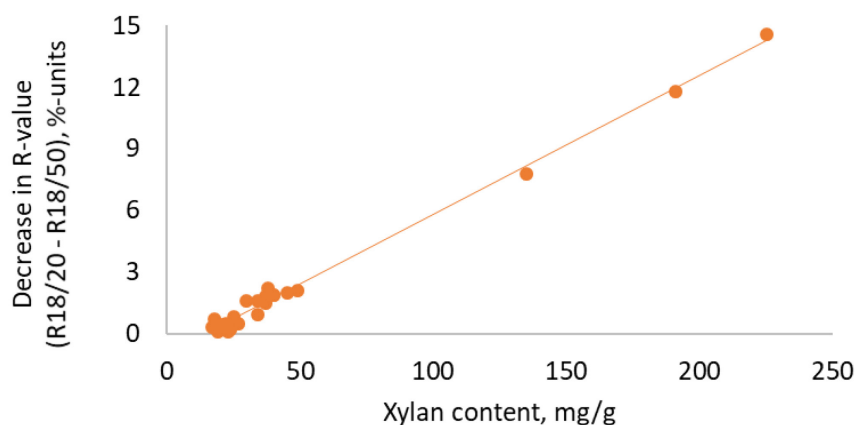
**Figure 34: Correlation between the residues after alkaline extraction with 18 wt% aq. NaOH at 20 and 50 °C (R18/20 and R18/50, respectively) for a variety of different hardwood (HW) and softwood (SW) pulps**

Accordingly, an increase of extraction temperature from 20 to 50 °C decreased yield for the nine analyzed softwood pulps with a data range of 98.4 - 86.7 % for R18/20 with 0.2 - 1.2 %-units, respectively. This linear decrease was valid for the wide range of the different analyzed softwood pulps, both for use as paper and

dissolving pulp. They contained 7 – 70 mg/g xylan and 8 – 66 mg/g mannan, had a viscosity of 448 – 669 ml/g and a PDI of 3.1 - 8.8. The parameters of xylan, mannan and PDI were found to have a weaker statistical influence on the R18/50 and could not improve the correlation. Viscosity had no statistically firm influence at all.

For hardwood pulps a correlation with  $R^2 = 0.9967$  and  $RMSE = 0.3$  was found when including the xylan content in mg/g (Equation 12 and simplified in Figure 35):

$$R18/50_{HW} = 13.8691 + 0.8674 \times R18/20_{HW} - 0.0707 \times \text{xylan content} \quad \text{Equation 12}$$



**Figure 35: Correlation between the xylan content in a variety of different hardwood pulps and the decrease of the residue after alkaline extraction with 18 wt% aq. NaOH at 50 compared to 20 °C (R18/20 - R18/50)**

Accordingly, an increase of extraction temperature from 20 to 50 °C decreased yield for the 24 analyzed hardwood pulps with a data range of 97.8 - 90.7 % for R18/20 and xylan content of 17 - 225 mg/g with 0.3 - 14.1 %-units. They contained 0 – 9 mg/g mannan, had a viscosity of 376 – 930 mg/g and a PDI of 3.1 – 7.6. The parameters of mannan and PDI were found to have a weaker statistical influence on the R18/50 and could not improve the correlation. Viscosity had no statistically firm influence at all.

A more universally valid correlation only based on the glucan content in mg/g, but with a much weaker precision ( $R^2 = 0.9657$ , RMSE = 0.8), could be identified for the whole data set of 34 pulps:

$$R18/50 = 15.007 + 0.0835 \times \text{glucan content} \quad \text{Equation 13}$$

#### 4.2.6 The effect on non-saccharides

The previous chapters focused on the changes of carbohydrates when exposing a pulp to alkaline extraction at conditions relevant for the industrial pretreatment of dissolving pulps. Even non-saccharide polymers in the pulp such as lignin-structures and substances extractable with organic solvents (extractives) will be affected by the treatment. Inorganic impurities in the alkali cellulose (AC) were not considered in this study as to a large extent they were extracted in the course of the sample preparation to gain the regenerated AC (rAC) by neutralization, washing and pressing. After pressing of the AC,  $\text{Na}^+$  will be the dominating metal ion in the AC. The ash content will increase in proportional to the alkali concentration applied and disproportional to the pressure applied.

The sample preparation, including neutralization, washing and pressing, leading to rAC is supposed to further purify the sample. Nevertheless, it was considered to be of interest to see if any differences in lignin and extractives content from different pulps could be detected. Lignin and extractives-related residues in rAC from seven market pulps - six dissolving wood pulps (DWP) and one paper pulp - were investigated (Table 6). Klason lignin – generally not detected or only present as traces in the pulp produced for dissolving purpose – was shown to be easily eliminated by the conditions of industrial alkalization. Substances spectrophotometrically detected and defined as acid-soluble lignin were not affected by the alkaline extraction of DWP. Ca. 4 mg/g resisted the alkaline extraction of the DWP. Accordingly, the substances forming the acid-soluble substances, denoted as acid-soluble lignin, resisted the neutralization, washing and pressing to rAC as well. This supports the assumption that rAC for the most part corresponds to the composition of AC. The small amounts of residual lignin structures possibly remaining in the ready DWP are supposed to be highly fragmented as result of the cooking process and are not seen to

interfere with further process steps of dissolution (Götze 1967). However, an influence on the optical properties of the textile fibers might be expected as they are known to be rich in chromophoric groups. Only the higher level of acid-soluble lignin detected in the paper pulp (*HWk-paper*) was reduced by the alkaline treatment.

**Table 6: Contents of Klason lignin, acid-soluble lignin and acetone extract in 7 different pulps and their regenerated alkali cellulose (rAC).**

<i>Sample<sup>a</sup></i>	<i>Klason lignin<sup>b</sup>, mg/g</i>	<i>Acid-soluble lignin<sup>c</sup>, mg/g</i>	<i>Acetone extract, %</i>
HWk 1a-EX	1	4	0.13
rAC	0	4	0.07
HWk 1a-ex	0	4	0.09
rAC	0	3	0.04
HWk 1a	0	4	0.04
rAC	0	3	0.03
HWs 1a	1	5	0.23
rAC	0	4	0.06
SWs 1	0	4	0.12
rAC	0	3	0.05
SWk-hp 1	0	3	0.32
rAC	0	4	0.02
HWk-paper	9	10	0.13
rAC	0	5	0.05

<sup>a</sup> HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity, the cipher code represents different pulp products according to Table 2, ex/EX – elevated content of extractives and xylan (ex < EX).

<sup>b</sup> According to SCAN-CM 71:09, corresponds to the insoluble residue after total acid hydrolysis

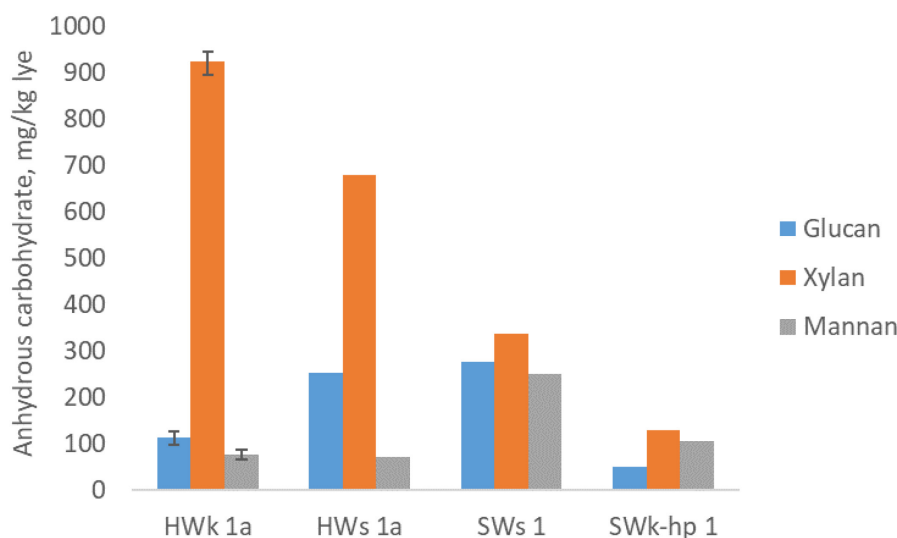
<sup>c</sup> According to SCAN-CM 71:09, acid-soluble substance which absorbs at 205 nm

The acetone-extractable compounds could be shown to be partly extracted by the alkaline treatment followed by neutralization, washing and pressing (Table 6). 0.02 – 0.07 % extractives were left in rAC. This study could not clarify at which time the extractives leave the process flow in viscose manufacturing. However, the results indicate that a reduced part of the extractives will end up in the extruded viscose fiber after passing both alkaline and acid treatments.

#### 4.2.7 Composition of press lye

The alkali extracted compounds from the pulp end up in the alkalization lye when producing alkali cellulose (AC). Under industrial conditions the alkalization lye is recirculated in the process and the extracted compounds concentrated up to a steady state level, depending on the specific purification technique, degree of system closure and alkali consumption strategy in the viscose mill. Mozdyniewicz et al. (2014) have analyzed the press lye from a hardwood sulfite pulp (R18 93.3 % and 3.1 % xylan) obtained after different treatment conditions. After treatment with 18 wt% aq. NaOH at 50 °C for one hour, the low molecular weight degradation products found in the lye mainly originated from cellulose, but also degradation products from xylan were detected. The polymeric carbohydrate fraction dissolved in the lye contained mainly anhydroxylose, but also anhydroglucose was found in this fraction. HPLC analysis showed that the DP of the polymeric carbohydrates in the lye was 25-30.

The present study considered the press lye of four different generic pulps. The trends found for polymeric carbohydrates (Figure 36) were as expected from the analysis of the initial pulps discussed above (4.1.3,). The error bars given for *HWk 1a*, originated from three experiments using the pulps *HWk 1a* and *HWk 1a-ex*, indicate a good repeatability for the alkalization experiments. Much xylan was found in the lye from hardwood (HW) pulps, most in the lye from *HWk 1a*, which was the pulp containing the most xylan from the beginning. In contrast, the lyes from softwood (SW) pulps contained more mannan, especially that derived from SW sulfite pulp. The sulfite pulps, with their high content of low molecular weight material (4.1.3), resulted in a lye with higher content of glucan. The high-purity pulp *SWk-hp 1* with its high cellulose content and low PDI had least detectable carbohydrates in the lye. Valid for all press lyes was that xylan was the dominating carbohydrate in press lyes independent of the type of pulp used and absolute amount of carbohydrates extracted (4.2.5).

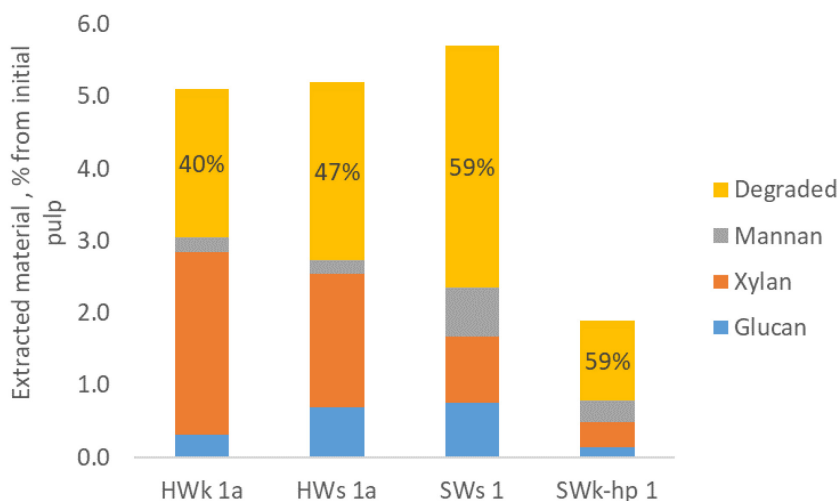


**Figure 36: Anhydro carbohydrates in the press lyes after alkalization of four different dissolving wood pulps. The error bars given for HWk 1a represent the minimum and maximum content from three experiments extracting the pulps HWk 1a and HWk 1a-ex. (HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity, the cipher code represents different pulp products according to Table 2)**

Comparing the amount of measured anhydro carbohydrates in the lye with the R18/50-value gave the possibility to estimate the level of degradation of the extracted carbohydrates (Figure 37). In the case of HW pulps, it was found that more than 50 wt% of the extracted carbohydrates still occurred as carbohydrates in the lye. The press lyes from the investigated SW pulps contained less than 50 % of the extracted material. The rest is supposed to be degraded to different hydroxy acids (Richards and Sephton 1957, Niemelä and Sjöström 1986, Knill and Kennedy 2003) and were not possible to detect with the quantification method applied. The pulps *HWk 1a-ex* and *SWs 1* were also analyzed for the composition of their regenerated alkali cellulose rAC (4.2.3, Figure 23). This made it possible to compare the carbohydrate composition of the extracted material according to the analysis of the rAC and the carbohydrate composition of the press lye. It could be shown that almost all xylan extracted from the *HWk 1a-ex* was detected as xylan in the lye (98 wt%), while only 75 wt% was detected in the lye from *SWs 1*. For glucan the development was contrary with 17 and 27 wt%, respectively, of the glucan detectable in the lye. It can be concluded that this study both confirms and extends the findings of Mozdyniewicz et al. (2014),



as different generic pulps were investigated. These data can be used to provide input for the recycling and upcycling strategies of the alkaline press lyes.



**Figure 37: Fractions extracted to the alkaline press lye of four different dissolving wood pulps.**

(HW – hardwood, SW – softwood, k – kraft, s – sulfite, hp – high purity, the cipher code represents different pulp products according to Table 2)

### 4.3 Structural properties of cold alkali extracted pulp in consideration of the drying procedure

This study investigated the structural differences of pulps with systematically-differing chemical compositions, representing paper pulp gradually developing towards dissolving pulp by means of varying its chemical composition. For this purpose, never-dried hardwood and softwood kraft paper pulps (HWk-paper, SWk-paper) were extracted in cold alkali of increasing concentration up to 8 wt% aq. NaOH. Table 7 shows the resulting chemical composition of the extracted never-dried pulps. As expected, alkaline extraction with increasing alkali concentration reduced xylan to a large extent while mannan was not affected to any large extent. This resulted, in the case of the xylan-rich HWk-paper, in a chemical composition corresponding to standard dissolving wood pulp (DWP) containing ca 5.5 % hemicellulose (*HWk-paper\_8*; 4.1.3). The more mannan-rich SWk-paper had ca 8 % hemicellulose remaining after the same treatment (*SWk-paper\_8*).

**Table 7: Chemical composition of never-dried cold alkali extracted paper pulps**

Alkali, wt% <sup>a</sup>	0	2.5	4	8	0	4	8
Component, mg/g	<i>HWk-paper<sup>b</sup></i>	<i>HWk-paper_2.5</i>	<i>HWk-paper_4</i>	<i>HWk-paper_8</i>	<i>SWk-paper</i>	<i>SWk-paper_4</i>	<i>SWk-paper_8</i>
Arabinan	0	0	0	0	7	4	2
Galactan	0	0	0	0	2	2	1
Glucan	744	796	854	941	850	878	915
Xylan	241	191	135	49	70	44	20
Mannan	3	4	4	5	64	66	57
Klason lignin	2	1	1	0	0	0	0
Acid-sol. lignin	9	8	7	5	7	6	5

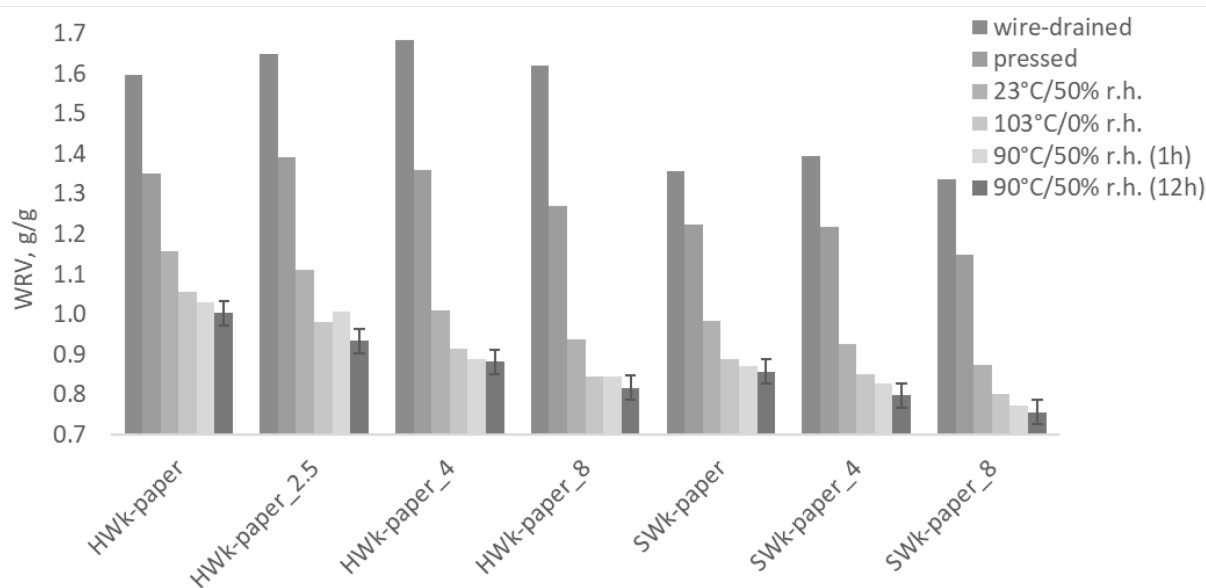
<sup>a</sup> concentration of aq. NaOH in wt% used for cold alkali extraction of the starting pulp

<sup>b</sup> HW – hardwood, SW – softwood, k – kraft

In order to systematically provoke structural changes, the extracted never-dried pulps were then dewatered according to six different procedures as described in chapter 3.2.3. Two procedures kept the never-dried state of the samples at a dry content of ca 30 % (wire drained) or ca 50 % (pressed). HWk-pulps had a dry content of 52 %, and SWk-pulps 55 % after pressing. The other four procedures included drying of the pressed pulps to 90 - 100 % dry content. The respective equilibrium moisture content was reached by exposing the pulps to different combinations of temperature and relative humidity (23°C/50% r.h. a.k.a. air-dried, 103°C/0% r.h. a.k.a. oven-dried, 90°C/50% r.h. during one hour, 90°C/50% r.h. during 12 hours) enabling evaporation of water. The hot and humid conditions (90°C/50% r.h.) were chosen with the intention of simulating the industrial applied conditions in the pulp drying section of a drying machine in a pulp mill.

HWk-pulps are generally known to have a higher WRV than comparable SWk-pulps. This is most likely a result of differences in higher specific surface area, porosity and content of hydrophilic hemicelluloses (2.2). This general difference also became visible in the present study (Figure 38). In the series of samples, the chemical composition was changed by extracting xylan in particular. As a

consequence of the gradually increased alkalinity in the extractions, the material became initially more porous. Furthermore, this porosity was expected to be affected by the different applied dewatering procedures causing hornification when pores collapse. The ranking for decreasing WRV and increasing hornification due to different dewatering procedures for all samples extracted at differing conditions was [wire drained] – [pressed] – [air-dried] – [oven dried] – [90°C/50% r.h. (1h), 90°C/50% r.h. (12h)]. This ranking can be interpreted as a measure of how severely the drying procedures affect the supramolecular structure. The clear decrease of WRV by 10 – 22 % for the pressed pulp compared with the wire-drained pulp is known from findings in literature showing that wet-pressing induces fiber hornification (Carlsson and Lindström 1984), and is comparable to data given by Luo et al. (2011). The increase in WRV of the wire-drained samples extracted with increasing amount of alkali indicated that extraction of xylan left interspaces accessible for additional water. However, the samples subjected to the most intense xylan extraction (*HWk-paper\_8*, *SWk-paper\_8*) decreased slightly in WRV. This indicated that the larger, or more numerous, interspaces created by extraction, leaving a more perforated



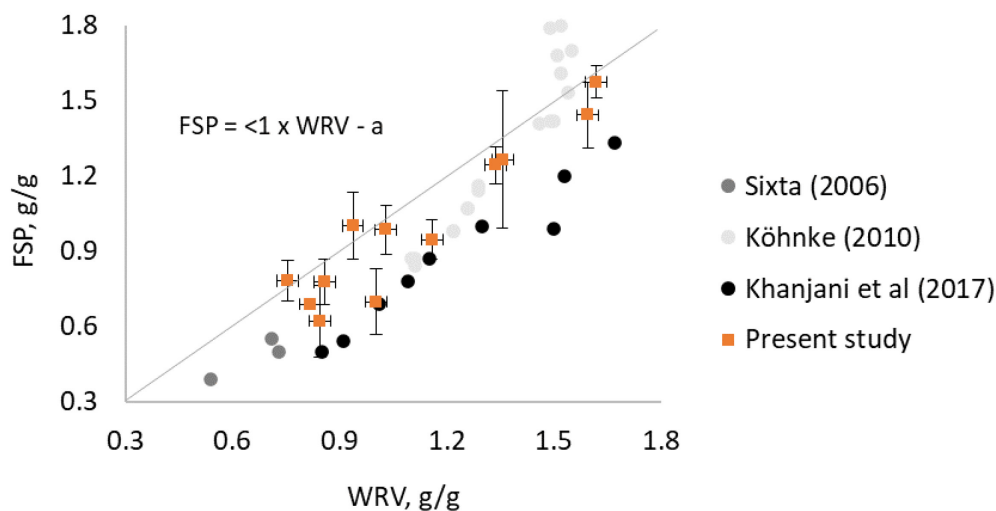
**Figure 38: Water retention value (WRV) measured on hardwood (HW) and softwood (SW) paper kraft pulp (k) extracted with cold alkali of different concentrations (0 - 2.5 - 4 - 8 wt% aq. NaOH) and dewatered/dried according to six different procedures. The accuracy of the measurement is given as  $\pm 0.03$  g/g.**

and weaker cell wall, had a tendency to hornify the fiber structure already at a dry content of 30 % after wire-drainage. For the pressed samples an increase in

WRV due to extraction of xylan could only be assumed for extraction with  $\leq 4$  wt% aq. NaOH. This might be connected to the higher forces acting on the structure when more dewatering was accomplished. When drying the pulps to  $> 90$  % dry content under conditions enabling evaporation of water from the fiber wall structure, pulps prepared with increasing concentration of alkali in the extraction showed a decreasing WRV. As expected, a clear difference could be shown between air-drying (23°C/50% r.h.) and the other drying procedures. Air-drying resulted in a ca 10 % higher WRV than the other evaporating drying procedures. Even if the three drying procedures applying higher temperatures resulted in relatively small differences in WRV, a clear tendency for lower WRV at longer drying times at higher humidity could be observed. Regarding the relative decrease in WRV obtained after wire-draining and more intense dewatering and drying procedures, this study clearly confirmed that hemicellulose impairs hornification. A steady decrease in WRV for all drying procedures was observed from unextracted to the highly-extracted samples.

Twelve samples out of the full sample matrix of 42 samples from this study were chosen to analyze the fiber saturation point (FSP), which measures exclusively the amount of water within pores of a diameter  $< 100$  nm. These represented the extremely extracted pulps *HWk-paper\_8* and *SWk-paper\_8* and its respective unextracted reference in wire drained, air-dried and 90°C/50%-treated condition. Their FSP values correlated clearly with WRV and the correlation was in general accordance with data given in literature (Sixta 2006b, Köhnke et al. 2010, Khanjani et al. 2017) (Figure 39). Nevertheless, the correlation was not as accurate as reported by Scallan (1972). Scallan has stated that WRV, measured with the centrifugal force 900 g instead of today's valid standard 3000 g, has been an exact measure of FSP up to values of 1.8 g/g, while highly-swollen samples with an FSP  $> 1.8$  have yielded a WRV  $< \text{FSP}$ . This tendency can be seen for the results presented by Köhnke et al. (2010) where samples with FSP  $> 1.5$  represent never-dried pulp with subsequently adsorbed glucuronoxylan. For these results, it has been argued that the WRV method has underestimated fiber swelling of those highly-swollen fibers due to the loss of intra-fiber water during centrifugation. Considering the data area FSP  $< 1.5$ , both the data from this present study and the reference data from literature answer the observation by Larsson et al. (2013) that WRV-based values actually overestimate the

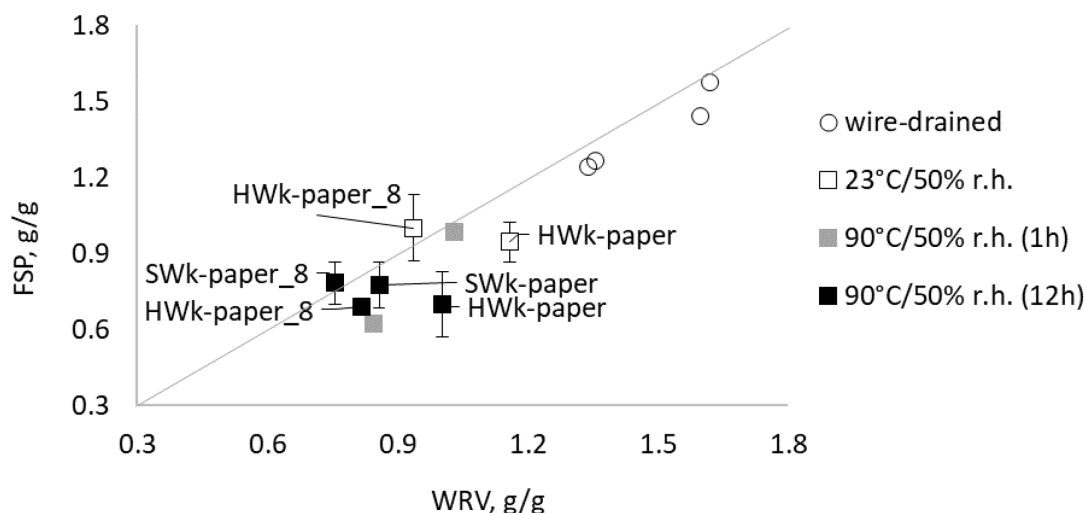
amount of water bound in the fiber wall pores ( $WRV > FSP$ ). This overestimation might be due to incomplete removal of the inter-fiber water.



**Figure 39: Comparison of results from determination of water retention value (WRV) and fiber saturation point (FSP) as derived from different references and the present study. General variation of WRV and the standard deviation of FSP are given for the present study**

**(Sixta 2006: Three market dissolving pulps; Köhnke et al. 2010: a series of softwood kraft paper pulp subsequently adsorbed with different amounts of glucuronoxylan in never-dried and air-dried state; Khanjani 2017: Various market pulps in never-dried and dried state.)**

A closer look at the data from the present study identified especially three highly extracted samples (...\_8), long-term dried with 90°C/50% and 23°C/50%, as outliers (Figure 40). They stood out with as high FSP as their unextracted reference and a high FSP compared to their WRV. No more investigations on this phenomenon were made.

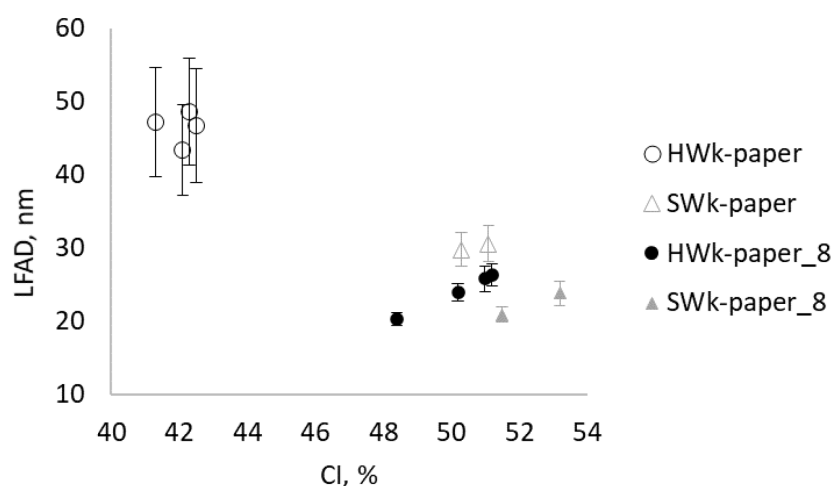


**Figure 40: Water retention value (WRV) versus fiber saturation point (FSP) for four different pulps dried with different procedures. For selected samples the standard deviation of FSP is given.**

Analysis of the CP/MAS  $^{13}\text{C}$ -NMR spectra measured on the same samples as analyzed for FSP delivered data on crystallinity index (CI), content of cellulose II (cell II), lateral fibril diameter (LFD), lateral fibril aggregate diameter (LFAD) and the specific surface area (SSA) according to LFAD (Appendix Table 18 and Figure 54).

The extracted samples generally had a higher level of CI than their reference pulps (Appendix Table 18). This might be partly due to extraction of amorphous cellulose, partly due to reorganization of disordered regions after extraction of other chemical components (Table 7). All pulps increased in CI with increased drying severity (wire-drained < 23°C/50% r.h. < 90°C/50% r.h. 1h < 90°C/50% r.h. 12h). This observation proves the tendency for increasing change of the original supramolecular structure under these conditions. Apart from HWk-paper, the samples showed a tendency for increased LFAD, especially the highly extracted ones (...\_8) (Figure 41). HWk-paper differed substantially from the other pulps regarding both CI and LFAD. This pulp had the lowest CI (ca 41 % to compare with ca 50 % for the other pulps), and LFAD showed a high absolute level of ca 45 nm and no straight development when exacerbating drying, while the relative standard deviation was almost three times as high compared to the other samples. It is assumed that the high content of hemicelluloses (24.4 %, Table 7) caused these outstanding properties of disordered structure. The

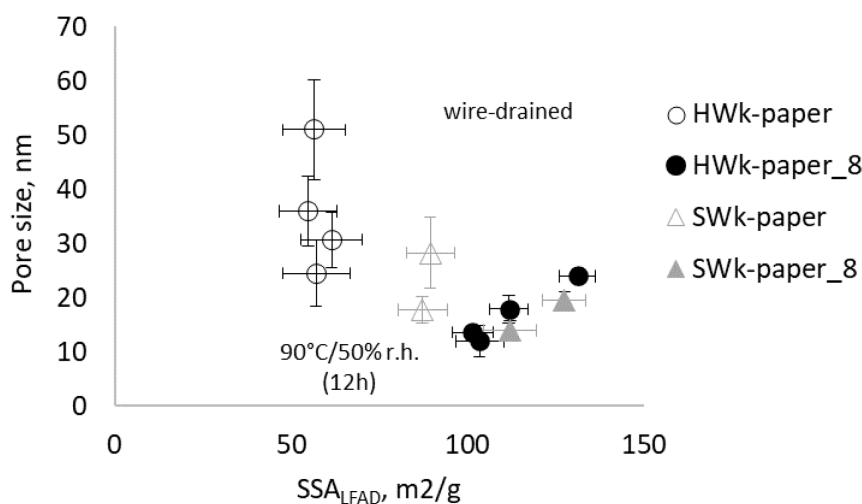
hemicelluloses still incorporated in the fibril aggregate structure were able to hinder distinct fibril aggregation and increase of CI during drying. It is also possible that the high content of hemicellulose changed the nature of the supramolecular structure in such a way that the algorithm applied on the NMR-data did not deliver reliable results. The high level of LFAD might accordingly be interpreted as illusive. However, both cold alkali extracted samples *HWk-paper\_8* and *SWk-paper\_8* resulted in a higher increase of CI and in a more significant tendency of increasing LFAD upon drying compared to their unextracted references. These properties can be explained by the removal of spacing hemicellulose making the cellulose polymers coming closer and aggregating to a higher extent upon drying. Newman (2004) has explained observations equal to the findings in this study as co-crystallization of adjacent cellulose molecules by irreversible hydrogen bonding after drying.



**Figure 41: Lateral fibril aggregate diameter (LFAD) and its standard deviation versus crystallinity index (CI), both determined by CP/MAS 13C-NMR, for hardwood (HW) and softwood (SW) paper kraft pulp (k) and its version after cold alkali extraction using 8 wt% aq. NaOH. One series represents samples dried at different conditions.**

Figure 42 summarizes the results from NMR and FSP by correlating the calculated average pore size to the calculated specific surface area ( $SSA_{LFAD}$ ). By this mathematical interpretation of the results discussed above it could be shown that the average pore size in all pulps decreased when exposed to drying. The pores were created during the initial pulping process, where mainly lignin

was removed from the fiber wall, yielding the two paper pulps. The pores in the respective cold alkali extracted never-dried pulps were expected to be larger than in the paper pulps. But, as the analysis of WRV indicated, a collapse of these large pores occurred already in the swollen state before dewatering, leading already in this initial phase of dewatering to a lower average pore size compared to the paper pulps. Again, the high standard deviation given for the average pore size of *HWk-paper* would imply that the absolute calculated size is too high. This is connected to the assumption that LFAD was overestimated due to the high content of hemicellulose.



**Figure 42: Specific surface area as calculated from lateral fibril aggregate diameter ( $SSA_{LFAD}$ ) determined by CP/MAS 13C-NMR versus average pore size determined by CP/MAS 13C-NMR and fiber saturation point (FSP) for hardwood (HW) and softwood (SW) paper kraft pulp (k) and its version after cold alkali extraction using 8 wt% aq. NaOH. One series represents samples dried at different conditions. The deviation given is the standard deviation of the analysis for each sample.**

Average pore size generally decreased by drying, while the specific surface area (SSA) stayed more constant the more hemicellulose was present in the sample (*HWk-paper* > *SWk-paper* > ...<sub>8</sub>). This implies that the chemical composition of pulps had an influence on the nature of hornification. Hornification due to partial collapse of pores leading to smaller pores, lower pore volume and finally lower WRV and FSP occurred in all samples. Hornification due to aggregation of fibrils occurred in pulps with high relative cellulose content, where



obstructing molecules had a low presence. Relating to the theory that co-crystallization occurs upon hornification, it is assumed that partial pore collapse comprises a less concentrated occurrence of co-crystallization in the fiber structure. In case of the occurrence of fibril aggregation, in this study measured as LFAD or  $SS_{LFAD}$ , co-crystallization covers large areas within the fiber wall.

Putting the drying study in the context of industrial pulp production, it can be assumed that inhomogeneous and varying drying performance on pulp drying machines might represent the span of the investigated drying procedures from air-drying to hot and humid drying. The performance of the drying process might depend on design and technology of the drying machine and inhomogeneities can be caused by uneven cross-machine moisture profile. This would result in too many dried sections in the web, while others remain more moist and the average moisture content would possibly still conform to the target moisture content. After baling and storage, the moist sections will approach equilibrium dryness which is assumed to correspond to air-drying. Accordingly, this study showed that the span in inhomogeneity of pulp drying would stand for a potential difference in hornification determined by a decrease in WRV of ca 14 % for all pulps investigated, independent of the degree of purification. Moreover, this study could estimate upcoming hornification due to increased purity. The WRV of HWk-paper samples decreased by 0.01 g/g for each 10 mg/g extracted hemicellulose, and SWk-paper samples decreased by 0.02 g/g for each 10 mg/g extracted hemicellulose.

#### 4.4 The conversion of wood pulp into carboxymethyl cellulose <sup>3</sup>

Market pulps from different processes, which are applied in different application areas (five dissolving wood pulps (DWP) and one paper pulp), were studied (Table 2). Long-fiber pulps, originating from softwood, were represented with a sulfite pulp (SWs 1) used in the production of standard viscose staple fibers (VSF), and a highly pure long-fiber kraft pulp (SWk-hp 1) used for special applications within cellulose derivatives. Short-fiber pulps,

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<sup>3</sup> This chapter is based on the publication "Influence of wood pulp quality on the structure of carboxymethyl cellulose" by C. Fechter and T. Heinze; published in Journal of applied polymer science, 2019-09-10, Vol.136 (34), p.47862-n/a

originating from hardwood, were represented by a sulfite and a kraft pulp used in VSF (*HWs 1a*, *HWk 1*) and a paper-grade kraft pulp (*HWk-paper*). *HWk-1* pulp with three degrees of variation was selected: standard quality (*HWk 1a*), elevated content of extractives (*HWk 1a-ex*), and elevated content of xylan and extractives (*HWk 1a-EX*).

In this study, different conditions of alkalization, ranging from excess to deficit, were used for the activation of pulps before CMC synthesis. The intention was to understand the reactivity and accessibility of different wood pulps. The content of insoluble matter and distribution pattern of substituents were evaluated as well.

The aim of the study was to understand the influence of the quality of wood pulp on the synthesis of carboxymethyl cellulose (CMC) samples and their properties. The pulps used were characterized in detail (Table 8).

#### **4.4.1 Pulp properties**

##### 4.4.1.1 Chemical composition of the pulps

The softwood kraft pulp with high purity (*SWk-hp 1*) had the highest glucan content. This was followed by a low content of other wood components owing to the especially adapted process conditions. The softwood sulfite pulp (*SWs 1*) used for standard viscose staple fibers (VSF) had the highest mannan content and a low xylan content as a result of the high mannan content of the raw material (~12 wt%, Sixta 2006a), and the acid process conditions, which degraded and extracted equal shares of the hemicelluloses. The hardwood kraft pulp for use in paper production (*HWk-paper*) had a high content of xylan and lignin common for strong paper grades. The three short-fiber kraft grades for VSF (*HWk 1a*, *HWk 1a-ex*, *HWk 1a-EX*) represented purified hardwood kraft pulp and contained 25 % more glucan than *HWk-paper*. The harsher alkaline process conditions in those kraft cooks left a xylan content of 3.4 to 4.5 wt% in the pulps derived from a raw material with a high xylan content above 30 wt% (Sixta 2006a). Moreover, the *HWk 1* series represented samples from the same wood source and the same process with different levels of extractives (Table 2 and Table 8). *SWs 1* and *HWk-paper* were found to have special properties in terms of metal content. *SWs 1* had apparently been produced in a process where

**Table 8: Summary of purity and structure-related properties of the investigated pulps.**

<i>Sample<sup>a</sup></i>		<i>SWk-hp</i> <i>1</i>	<i>SWs</i> <i>1</i>	<i>HWs</i> <i>1a</i>	<i>HWk</i> <i>1a</i>	<i>HWk</i> <i>1a-</i> <i>ex</i>	<i>HWk</i> <i>1a-EX</i>	<i>HWk-</i> <i>paper</i>
Glucan	mg/ g	980	960	968	956	954	944	746
Xylan	mg/g	7	14	23	34	37	45	225
Mannan	mg/g	8	21	3	5	4	6	3
Klason lignin	mg/g	0	0	1	0	0	1	9
Acid sol lignin	mg/g	3	4	5	4	4	4	10
Extractives <sup>b</sup>	%	0.32	0.12	0.23	0.04	0.09	0.13	0.13
Ash	%	0.10	0.08	0.06	0.04	0.04	0.04	0.62
Ca	ppm	39	25	7	41	43	34	379
Mg	ppm	6	243	4	53	63	61	725
Na	ppm	465	124	503	123	85	n.d.	1250
Intrinsic viscosity	ml/g	641	560	516	412	391	440	780
DPw <sup>c</sup>		2104	1752	1414	1060	1048	1062	2752
PDI <sup>d</sup>		3.1	6.4	5.9	3.2	3.0	3.2	7.6
CI <sup>e</sup> (WAXS)	%	50	70	67	69	67	66	62
Cell II (WAXS)	%	33	4	3	3	7	3	-3
Crystallite length (WAXS)	nm	6.3/6.3 <sup>g</sup>	5.7	5.3	5.4	5.5	5.6	5.6
Crystallite width (WAXS)	nm	4.5/5.4	4.3	3.6	4.1	4.9	3.4	3.3
CI (Raman)	%	53	46	47	48	48	48	47
Cell II (Raman)	%	28	3	3	3	6	5	4

<sup>a</sup> SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, the cipher code represents different pulp products according to Table 2, ex/EX - high extractives and xylan (ex < EX)

<sup>b</sup> Extractives > 0.2 % most probably originated from an additive

<sup>c</sup> Weight average degree of polymerization determined with GPC-MALS

<sup>d</sup> Polydispersity index determined with GPC-MALS

<sup>e</sup> Crystallinity index

<sup>g</sup> Dimension of respective phase (Cell I and Cell II). The two results are based on resolvable reflexes of the respective phase.

magnesium had been added as it had a higher magnesium content (4.1.5). As the production of *HWk-paper* was not optimized for purity, very high contents of several kinds of metals, reflected by a ten-fold higher ash content than the dissolving pulp, were detected.

#### 4.4.1.2 Structural properties of the pulps

The alkaline cooking conditions applied in the kraft process lead to a well-swollen cell wall and homogeneous degradation over the cross section (Duan et al. 2015, Fengel and Wegener 1989, Almlöf 2010). The molecular weight distribution expressed as polydispersity index (PDI) becomes narrow as soon as the hemicelluloses have been removed to a high extent. This could be shown for *SWk-hp1*, *HWk 1a*, *HWk 1a-ex*, *HWk 1a-EX*, while *HWk-paper* had a broad PDI due to the high share of short-chained xylan. Adapting the cooking conditions for low hemicellulose content (*HWk 1a*, *HWk 1a-ex*, *HWk 1a-EX*) caused the molecular weight, expressed as degree of polymerization (DP as intrinsic viscosity and weight average degree of polymerization (DP<sub>w</sub>)), to become low due to extended hydrolysis reactions. The alkaline process conditions of the kraft process could not be related to the distinct abundance of Cell II (4.1.6). Anyhow, a slightly elevated content of Cell II could be detected in *HWk 1a-ex*. The high DP found in connection with the high glucan content (i.e. high cellulose content) of *SWk-hp 1* was due to the especially adapted process conditions, which were also responsible for the high share of Cell II in the pulp found. This property combination is most likely due to harsh alkali extraction (4.1.6). The acid-cooked sulfite pulps (*SWs 1*, *HWs 1a*), where less swelling leads to more inhomogeneous treatment at the same time as acid hydrolysis decreases the molecular weight randomly, had a high DP and a broad PDI. No transformation to Cell II was expected, and the level found was comparable to that of the standard kraft pulps. Neither CI nor the crystallite dimensions differed significantly among the standard kraft and sulfite pulps. A slight tendency towards a higher CI and larger crystallites was found for *SWs 1*, but this could not be related to any generic pulp property or process history. The low CI of *HWk-paper* can be explained by the high xylan content as xylan acts as a spacer between cellulose chains. The CI of *SWk-hp 1* found using the Raman

analysis and WAXS differ extremely in relation to the other samples. It can be assumed that Cell II interfered with the spectrum making the result less reliable.

#### 4.4.2 CMC synthesis

CMC was prepared in two stages in aqueous-alcoholic systems. The cellulose (pulp) was alkalinized with aqueous sodium hydroxide (NaOH) of different concentrations in the range from 3 to 15 wt% and subsequently reacted with sodium monochloroacetate (SMCA). The change in the concentration of the aqueous NaOH meant that the amount of water available during alkalization and derivatization had changed. Thus, the ratio between polar liquid and the less polar slurry medium (isopropanol) must be considered as well. The resulting net-weights and molar ratios for the solvent and reagent are summarized in Table 9.

**Table 9: Trial settings CMC synthesis of 5 g pulp.**

<i>Reaction medium</i>	<i>aq.</i>	<i>H<sub>2</sub>O</i>	<i>H<sub>2</sub>O: CH(CH<sub>3</sub>)<sub>2</sub>OH</i>	<i>AGU : NaOH : ClCH<sub>2</sub>COONa</i>
<i>aq. NaOH</i>	<i>NaOH</i>			
<i>(wt%)</i>	<i>(g)</i>	<i>(g)</i>	<i>(w : w)</i>	<i>Molar ratio</i>
3	2.09	67.58	1 : 1.7	1 : 1.7 : 1.7
5	2.09	39.71	1 : 2.9	1 : 1.7 : 1.7
15	2.09	11.84	1 : 9.9	1 : 1.7 : 1.7

The concentration of the aqueous NaOH is known to have a strong influence on the etherification reaction of cellulose. An incomplete transformation of cellulose to sodium cellulose (Na-Cell) lowers the reactivity of the pulp and may yield CMC of a lower degree of substitution (DS) and/or uneven distribution of the substituents within the biopolymer chain (Yokota, 1985).

Furthermore, the presence of an excess of water should be omitted as it will promote the hydrolysis of SMCA. This means that the trial in the presence of 3 wt% aq. NaOH challenges the synthesis in two ways. The low alkali concentration will swell the cellulose less (2.3.1) and more free water will reduce the concentration of effective SMCA.

Even the ratio between isopropanol and water is of importance. As isopropanol is a poor solvent for NaOH, a two-phase system occurs. Therefore, isopropanol acts as a swelling-restrictive agent and might not permit full hydration of the cellulose chain (Lopez et al. 2018).

By varying the alkali concentration with the available water volume, the trial setup varied several process parameters, which had counteracting effects on the DS. Little water means a high alkali concentration, more complete conversion to Na-Cell, and more swelling and higher SMCA stability, and little water also means more non-polar solvent, which restricts swelling.

The CMC samples prepared in the presence of 5 or 15 wt% aq. NaOH yielded CMC with a DS corresponding to commercially available qualities (Heinze and Koschella, 2005) (Table 10). The DS of 1.32 – 1.37 of the CMC obtained after activation with 15 wt% aq. NaOH corresponds to a reaction efficiency of 80 %. This high value shows that the low ratio of water : alcohol did not limit the reaction. The tight span shows that the different preconditions in the pulps had no clear effect on the DS in the cellulose. The span of 0.71 – 0.77 obtained for the DS in the dissolving pulps after activation with 5 wt% aq. NaOH allows the same conclusion. But, the low-purity, paper pulp based CMC *HWk-paper.5* had a DS of only 0.64 showing that reactivity on the cellulose was inherited.

Due to less activation of the pulp, preparation of CMC by activation of the pulps with aqueous NaOH of a concentration of 3 wt% (*SWs 1.3 and HWs 1a.3*, Table 10) led to a drop in DS below 0.2. The studies that applied 3 wt% aq. NaOH were limited to those pulps that gave CMC with the lowest content of insoluble matter at higher concentrations of aqueous NaOH (*SWs 1, HWs 1a*) (4.4.3.2).

**Table 10: Quality data from CMC produced from seven different pulps.**

<i>CMC Sample-ID<sup>a</sup></i>	<i>Aq. Alkali wt%</i>	<i>DS (HPLC)</i>	<i>Visco-sity mPa s</i>	<i>Visual appearance of the solution</i>	<i>Ins.<sup>b</sup> matter wt%</i>	<i>Visual appearance of the deposit</i>
SWk-hp 1.5	5	0.76	114	clear, some fiber lint	1.4	jelly
SWk-hp 1.15	15	1.35	84	clear, some fiber lint	0.7	jelly
SWs 1.3	3	0.16	5	Milky	81.8	fibrous, white
SWs 1.5	5	0.77	49	clear, some fiber lint	0.1	-
SWs 1.15	15	1.37	44	clear, some fiber lint	0.2	-
HWs 1a.3	3	0.18	4	Milky	86.5	fibrous, white
HWs 1a.5	5	0.72	51	clear, some fiber lint	0.2	-
HWs 1a.15	15	1.32	36	clear, some fiber lint	0.1	-
HWk 1a.5	5	0.74	45	clear, some fiber lint	5.3	jelly
HWk 1a.15	15	1.33	32	clear, some fiber lint	0.7	-
HWk 1a-ex.15	15	1.34	29	clear, some fiber lint	0.4	-
HWk 1a-EX.5	5	0.71	53	clear, some fiber lint	0.5	-
HWk 1a-EX.15	15	1.37	31	clear, some fiber lint	0.4	-
HWk-paper.5	5	0.64	110	turbid, greyish	25.7	jelly
HWk-paper.15	15	1.33	80	clear to greyish, fibers	0.3	jelly

<sup>a</sup> SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, the cipher code represents different pulp products according to Table 2, ex/EX - high extractives and xylan (ex < EX), 3/5/15 relates to the alkali concentration during derivatization

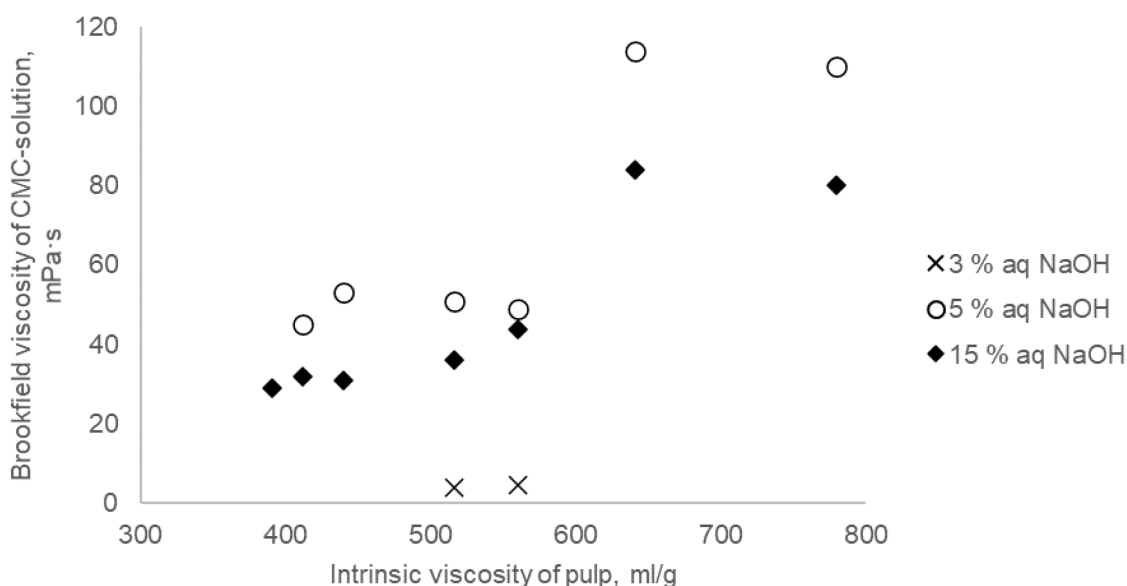
<sup>b</sup> Ins. – insoluble

#### 4.4.3 CMC properties

##### 4.4.3.1 Viscosity of the CMC-solutions

The viscosity of the solution of a carboxymethylated polysaccharide is a key property when used as a thickener and is highly influenced by the DP of the pulp used. The CMC synthesized in the presence of 15 wt% aq. NaOH (*SWk-hp 1.15*, *SWs 1.15* ... *HWk-paper.15*) dissolved well, resulting in good correlation between the intrinsic viscosity of the pulp used and the viscosity of the aqueous solution of the CMC (Figure 43). It was assumed that CMC synthesized in the

presence of 15 wt% aqueous NaOH and 5 wt% aq. NaOH (*SWk-hp 1.5*, *SWs 1.5 ... HWk-paper.5*) possessed an even distribution of the carboxymethyl groups (Heinze and Liebert 2012). However, the thickening behavior of the CMC obtained in the presence of 5 wt% aq. NaOH (*SWk-hp 1.5*, *SWs 1.5 ... HWk-paper.5*) increased significantly as the lower DS exhibited longer blocks of unsubstituted cellulose. Unsubstituted blocks promoted the association between the chains, which led to an increase in the viscosity of the solution (Lopez and Richtering 2019). This phenomenon of the formation of a three-dimensional network might even lead to more undissolved elements and a decrease in solubility (4.4.3.2).



**Figure 43: Dependence of the intrinsic viscosity of the starting pulp on the viscosity of an aqueous solution (1 %) of carboxymethyl cellulose (CMC) synthesized under different conditions (Table 9). Degree of substitution (DS) for 3, 5 and 15 wt% aq. NaOH is 0.3, 0.7 - 0.8, and 1.3 – 1.4, respectively.**

CMC prepared from *HWk-paper* (*HWk-paper.5* and *HWk-paper.15*) did not produce thickening as expected based on its high DP (Table 8). The lower DS obtained for the *HWk-paper* in combination with a high level of xylan probably deteriorated the performance of the CMC. Moreover, the greyish to turbid appearance of the solution indicates that the highly elevated content of divalent cations endured the neutral wash of the CMC at least partly and additionally



interfered with the thickening of the solution (Amtex 2014). The thickening is hindered by less expansion of the polymer in the presence of divalent cations, which is caused by a reduction in intrachain electrostatic repulsion.

CMC prepared in the presence of a 3 wt% aq. solution of NaOH (*SWs 1.3 and HWs 1a.3*) and a DS below 0.2 yielded a fibrous suspension where only a minor part of the cellulose derivative had been dissolved and was not able to build a strengthening three-dimensional network. The viscosity measured corresponds to the viscosity of water.

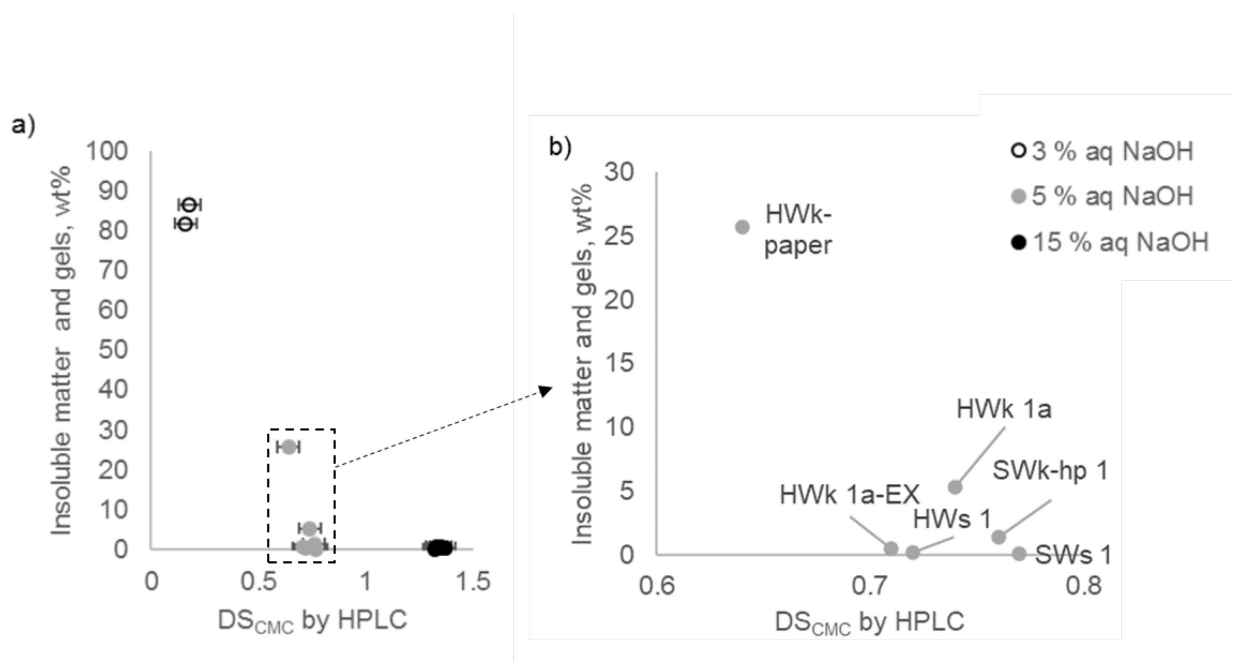
#### 4.4.3.2 Insoluble matter and gels of the CMC solution

In commercial high purity-grade CMC, a common share of insoluble matter and gels is ca. 0.5 wt% (specified for DS 0.95) (Tuyet et al. 1981). This study showed that this magnitude can be reached with any investigated raw material when favorable synthesis conditions with 15 wt% aq. alkali are chosen. Contrariwise, CMC prepared with 3 wt% aq. NaOH resulting in very low DS and giving no thickening when aimed to dissolve in water resulted in more than 80 wt% insoluble matter and gels (see Figure 44).

At synthesis conditions resulting in DS 0.64 - 0.77 (5 wt% aq. NaOH), which is near the dissolving limit of CMC in water, differences between the investigated pulps could be found. Low purity pulp (*HWk-paper*) showed an effect on solubility, which resulted in CMC with insoluble matter and gels significantly above a commercially acceptable level. *HWk-paper* represented a raw material with high DP and low purity in terms of carbohydrate composition (xylan and lignin) and inorganics. At a DS lower than the other pulps in the series and a lower thickening behavior as expected, this sample yielded considerable amounts of insoluble matter. The greyish appearance of the solution suggests that chromatic impurities caused this behavior. Tuyet et al. (1981) have proposed that lignin in mechanical pulp does not prevent the carboxymethylation of carbohydrates but prevents carboxymethylated carbohydrates from dissolving in water. This phenomenon was confirmed by the present results. *SWk-hp 1* represented a raw material with high DP and high content of the allomorph Cell II (66 % of the crystalline part). Both properties

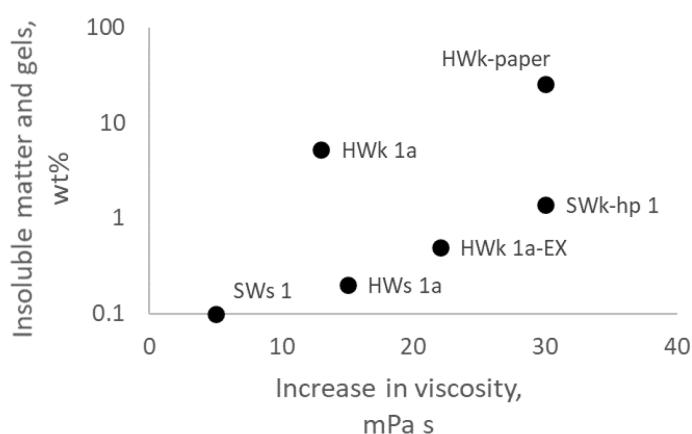
were expected to contribute to an elevated amount of insoluble matter, which would give a clear gel.

Considering the entirety of the investigated pulps carboxymethylated in the presence of 5 wt% aq. alkali, a ranking based on insoluble matter and gels supports the assumption that sulfite pulps are more reactive than kraft pulps, yielding a more even derivatization and higher solubility. Whereas it was expected that *HWk-paper* would have the worst performance, the poor performance of *HWk 1a* was surprising. *HWk 1a-EX*, with its lower purity of xylan and extractives, performed significantly better. Only the slightly higher CI of *HWk 1a* could indicate a lower reactivity of this sample (Table 8). The slightly higher CI might originate in the high purity that causes the remaining cellulose structure to aggregate to a greater extent under alkaline process conditions during pulp production. This would make the structure less available. The only measured property which might explain the good solubility of *HWk 1a-EX* would be the low crystallite width in the pulp.



**Figure 44:** a) Solubility of different carboxymethylated pulps produced with different concentrations of aqueous NaOH correlated to the degree of substitution (DS) in carboxymethyl cellulose (CMC) using HPLC. b) Magnification of 2: a showing samples prepared with 5 wt% aq. NaOH (SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, the cipher code represents different pulp products according to Table 2, E - high extractives, X - high xylan)

Relating the increase of viscosity when derivatizing at 5 compared to 15 wt% aq. NaOH to the amount of insoluble matter and gels, the assumption done in 4.4.3.2, that the increase of viscosity leads to a decrease in solubility, can be mainly confirmed (Table 10, Figure 45). The paper pulp *HWk-paper* increased comparably little in viscosity compared to the absolute amount of insoluble matter when derivatizing at 5 wt% aq. NaOH, which might be explained with the high level of impurities influencing viscosity in different ways (4.4.3.1). It would be interesting to further investigate the real reason for the high amount of insoluble matter and gels for the comparably pure pulp *HWk 1a*. The indications given by the difference in supramolecular structure (CI and crystallite width) do not seem to be significant when considering the findings done in 4.1.6.



**Figure 45: Increase of viscosity of dissolved CMC when derivatizing different pulps with 5 compared to 15 wt% aq. NaOH in relation to the content of insoluble matter and gels when derivatizing at 5 wt% aq. NaOH**

(SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, the cipher code represents different pulp products according to Table 2, E - high extractives, X - high xylan)

#### 4.4.3.3 Structural properties of the CMC

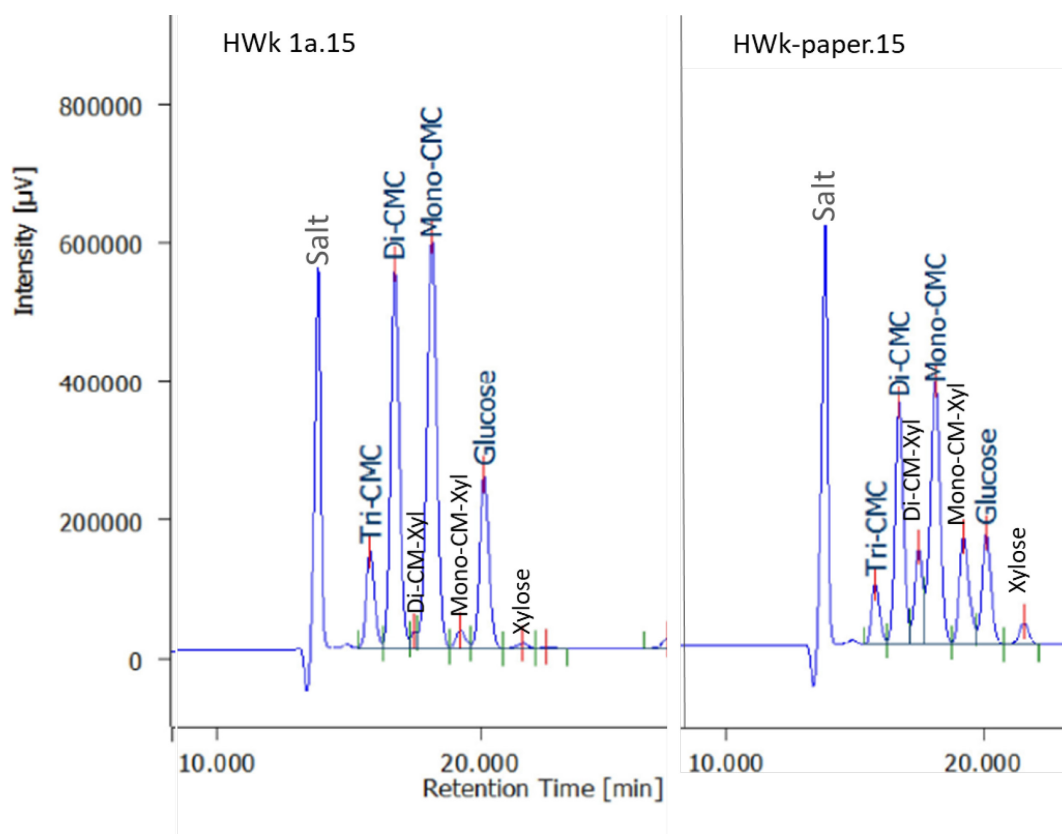
The DS values of the carboxymethylated pulps were determined by means of HPLC and  $^1\text{H}$  NMR spectroscopy after the hydrolytic degradation of the chain (Table 11). The different repeating units present in CMC were distinguished using HPLC, i.e. the mono-, di-, and tri-carboxymethylated units and glucose as

well as mono- and di-CM-xylose and unmodified xylose. Only the HPLC signals derived from the CMC were included in the calculation of DS ( $DS_{CMC}$ ), Figure 46.

**Table 11: Degree of substitution (DS) of carboxymethylated cellulose (CMC) produced from different pulps.**

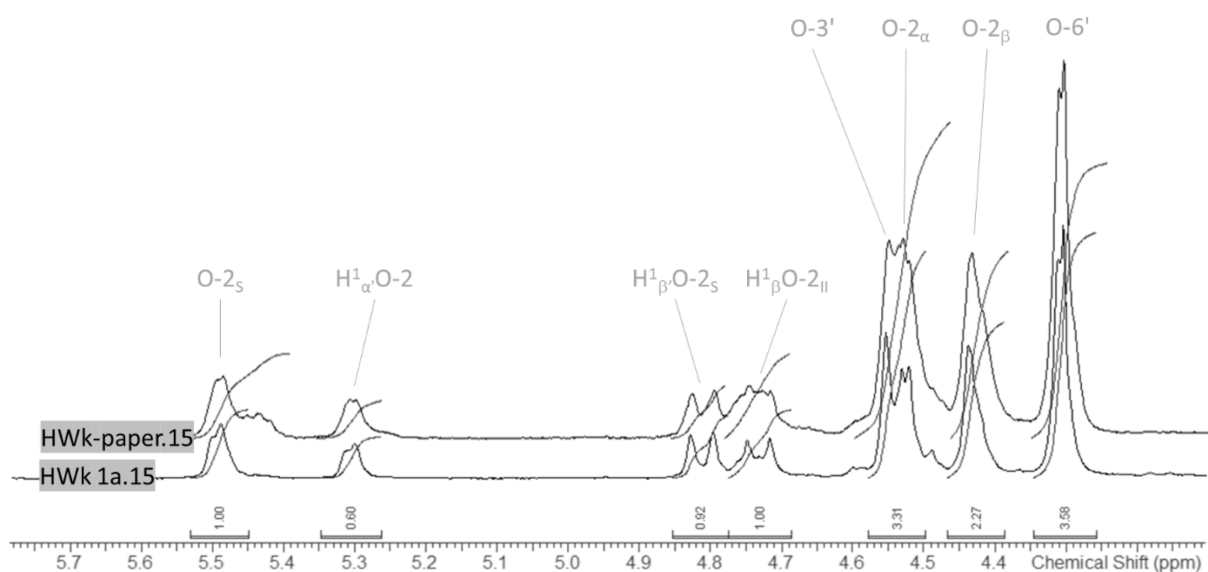
CMC Sample-ID <sup>a</sup>	Aq. alkali %	$DS_{CMC}$ mono	$DS_{CMC}$ di	$DS_{CMC}$ tri	$DS_{CMC}$ total (HPLC)	DS Pos 2	DS Pos 3	DS Pos 6	DS total (NMR)
SWk-hp 1.5	5	0.41	0.31	0.04	0.76	n.d.	n.d.	n.d.	n.d.
SWk-hp 1.15	15	0.40	0.69	0.26	1.35	0.58	0.24	0.52	1.34
SWs 1.3	3	0.14	0.03	0.00	0.16	0.12	0.12	0.11	0.35
SWs 1.5	5	0.41	0.32	0.04	0.77	n.d.	n.d.	n.d.	n.d.
LF.15	15	0.42	0.70	0.25	1.37	0.57	0.29	0.52	1.38
HWs 1a.3	3	0.15	0.03	0.00	0.18	0.11	0.13	0.11	0.35
HWs 1a.5	5	0.41	0.28	0.03	0.72	n.d.	n.d.	n.d.	n.d.
HWs 1a.15	15	0.43	0.66	0.23	1.32	0.54	0.28	0.49	1.31
HWk 1a.5	5	0.40	0.30	0.04	0.74	n.d.	n.d.	n.d.	n.d.
HWk 1a.15	15	0.42	0.67	0.24	1.33	0.55	0.29	0.51	1.35
HWk 1a-ex.15	15	0.42	0.68	0.24	1.34	0.57	0.29	0.52	1.38
HWk 1a-EX.5	5	0.40	0.28	0.03	0.71	n.d.	n.d.	n.d.	n.d.
HWk 1a-EX.15	15	0.42	0.70	0.25	1.37	0.56	0.33	0.53	1.42
HWk-paper.5	5	0.38	0.23	0.03	0.64	n.d.	n.d.	n.d.	n.d.
HWk-paper.15	15	0.42	0.67	0.24	1.33	0.51	0.43	0.51	1.45

<sup>a</sup> SW - softwood, HW - hardwood, s - sulfite, k - kraft, hp - high purity, ex/EX - high extractives and xylan (ex < EX)

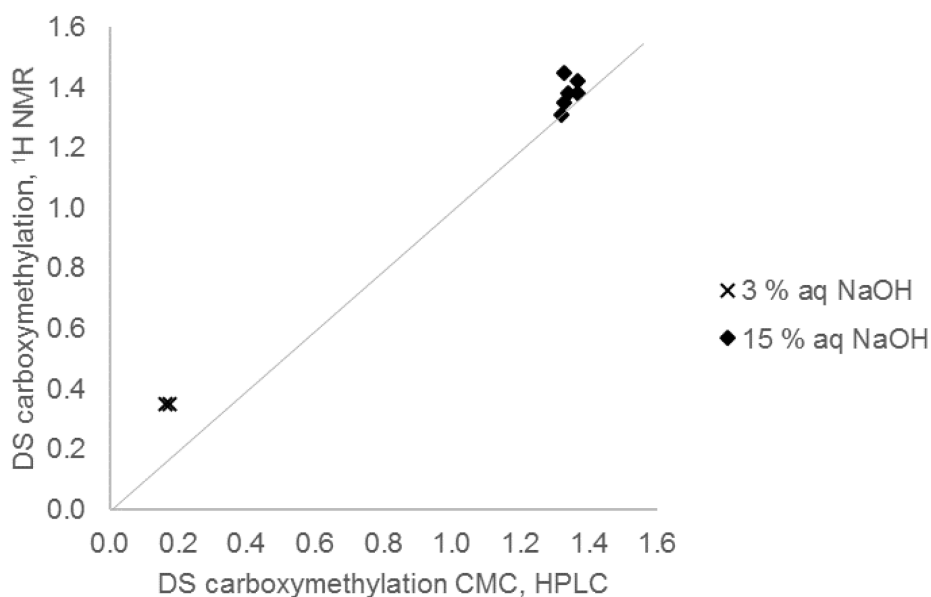


**Figure 46: HPLC chromatograms of carboxymethyl cellulose (CMC) obtained from VSF-standard pulp (HWk 1a.15) and paper pulp (HWk-paper.15) in the presence of 15 wt% aq. NaOH.**

$^1\text{H}$  NMR spectra were used to evaluate the partial DS at positions 2, 3, and 6 of the repeating units. No algorithm is currently available to reveal whether Positions 2 and 3 belong to an anhydroglucose unit (AGU) or an anhydroxylose unit (AXU). Figure 47 illustrates the small differences in chemical shifts at 5.45 and 4.75 ppm, which might be due to an elevated xylan content. This issue explains why  $\text{DS}_{\text{NMR}}$  was higher than the  $\text{DS}_{\text{CMC}}$  from HPLC was, see Figure 48. Non-cellulose carbohydrates, i.e. hemicelluloses, consumed the SMCA and increase the total DS. This behavior was even more pronounced at a lower degree of swelling in the cellulose structure due to the low alkali content during synthesis (3 wt% aq. NaOH). The  $\text{DS}_{\text{NMR}}$  was twice as high as  $\text{DS}_{\text{HPLC}}$ . Considering HWk-paper, containing a high amount of xylan which is able to consume SMCA, this pulp showed the highest difference between  $\text{DS}_{\text{NMR}}$  and  $\text{DS}_{\text{HPLC}}$  when derivatizing with 15 wt% aq. NaOH and the same can be assumed when derivatizing with 5 wt% aq. NaOH yielding low quality CMC.



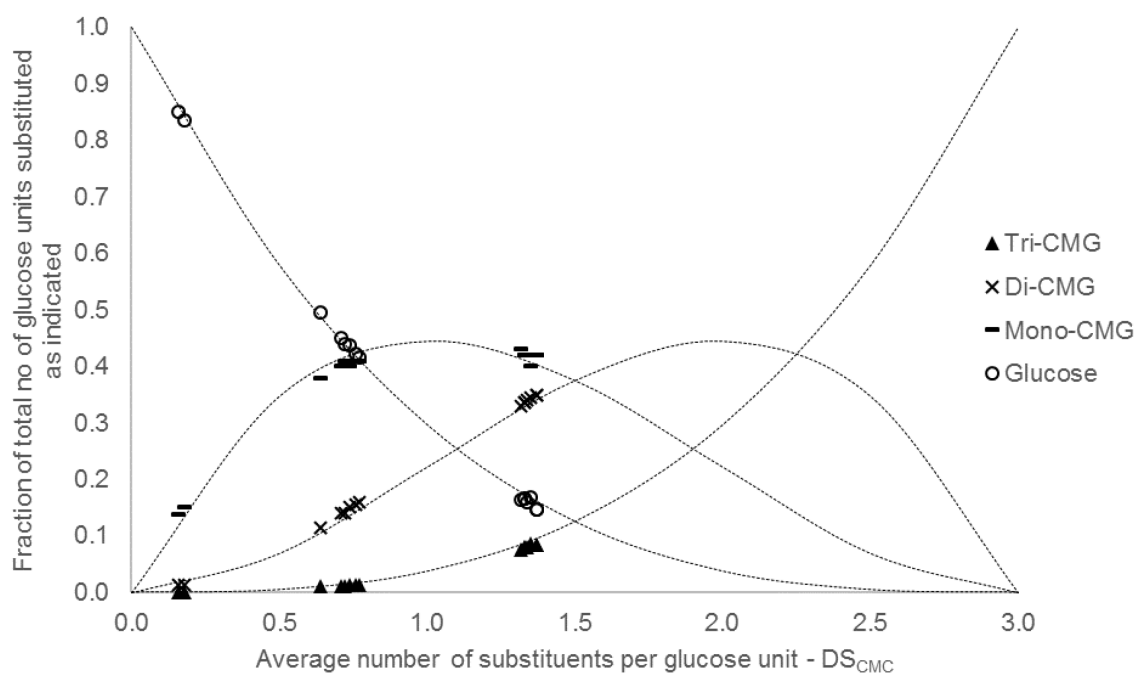
**Figure 47:**  $^1\text{H}$  NMR-spectra of carboxymethylated pulp obtained from VSF-standard pulp (HWk 1a.15) and paper pulp (HWk-paper.15) in the presence of 15 wt% aq. NaOH.



**Figure 48:** Degree of substitution (DS) of carboxymethyl cellulose (CMC) obtained from different pulps in the presence of 3 or 15 wt% aq. NaOH.

All substitution patterns of the investigated CMC determined with HPLC corresponded to the statistical distribution according to the Spurlin Equation (Spurlin 1939), assuming a rate constant ratio of 1 : 1 : 133 (Figure 49). More than

80 % of the AGUs were substituted in a CMC with a DS of >1.3 synthesized with 15 wt% aq. NaOH. As the substituted units are the starting point of dissolution in water, almost the entire molecule chain interacted with the solvent and dissolved all CMC obtained from the pulps. Less than 60 % of the AGUs were substituted using a 5 wt% concentration of aq. NaOH and decreasing the DS to < 1.0. According to the findings done for insoluble matter and gels, this level might lead to a steric hinder when CMC from pulps with an impeded availability of its cellulose is dissolved. This obviously occurred in the *SWk-hp 1* sample with its high content of Cell II, and it occurred in the *HWk-paper* sample with its high content of hemicellulose and lignin. Only the latter led to a significant lower DS of the cellulose.

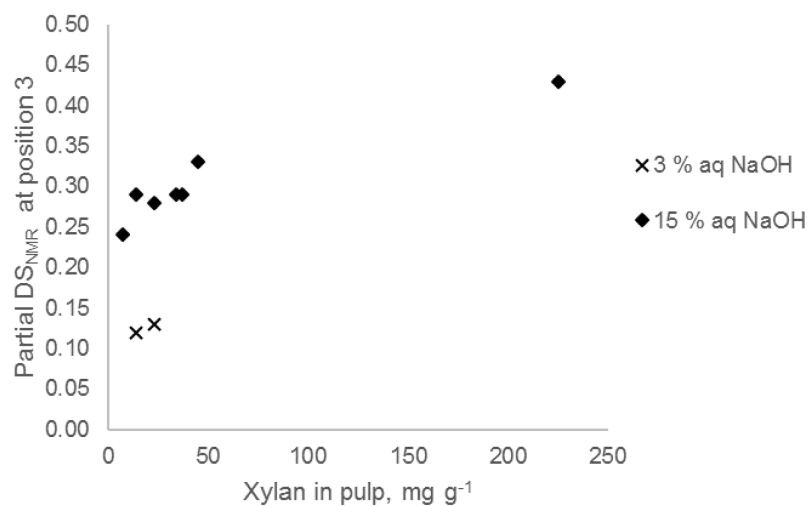


**Figure 49: Mole fractions of different repeating units of carboxymethyl cellulose (CMC) prepared from different pulps (see Table 11) versus average degree of substitution per anhydroglucose unit. The dotted lines represent the statistical substitution of cellulose ether according to Elias33 assuming a rate constant ratio of 1 : 1 : 1, cf. Spurlin (1939).**

The determination of DS using  $^1\text{H}$  NMR spectroscopy after hydrolytic chain degradation showed different substitution patterns for the position at the repeating unit (partial DS) for the carboxymethylated pulp prepared in the

presence of different lye concentrations. The three hydroxyl groups of each AGU, i.e. the primary hydroxyl group at Position 6 and the two secondary ones at Positions 2 and 3, were etherified to different extents. It was found that the reactivity of the hydroxyl groups towards carboxymethylation in 15 wt% aq. NaOH decreased in the following order; Position 2 > Position 6 >> Position 3, which is in agreement with the findings published by Baar et al. (1994). This pattern was less pronounced for the xylan rich HWk-paper sample. Niemelä and Sjöström (1989) have studied CMC synthesis from birch kraft pulp containing 20 % xylan. Those authors have found the ratio for Position 2 : Position 3 : Position 6 to be 3.1 : 1 : 2.6 in the CMC part of the derivatized pulp. For the reacted xylan (CMX), the ratio for Position 2 : Position 3 has been 2.5 : 1. This ratio was not confirmed in the present study where a total ratio for CMC and CMX was determined to be 1.2 : 1 : 1.2 for the corresponding HWk-paper sample using the favorable conditions of 15% alkali. This means that the OH groups in the HWk-paper sample had more even reactivity with a twice as reactive Position 3 compared to the findings of Niemelä and Sjöström. The reactivity at Positions 2 and 6 decreased to the level of Position 3 for the investigated sulfite pulps HWs 1a and SWs 1 at lower DS when 3 wt% aq. NaOH was used. The occurring variation of  $DS_{NMR}$  was rooted in the variation of DS at Position 3, which correlates positively to the xylan content in the pulp, see Figure 50. This resulted in significantly higher DS at Position 3 with high xylan content and illustrates how the more accessible xylan was substituted at this position, which is the least reactive one in the cellulose part of the sample.





**Figure 50: Dependence of the degree of substitution (DS, determined using NMR) at Position 3 of carboxymethylated polysaccharide on xylan content in pulp. The CMC samples were prepared from different pulps (see Table 8 and Table 11) in the presence of different concentrations of aqueous NaOH.**

## 5 Summary – implications and recommendations

This thesis provides a comprehensive description and comparison of present market dissolving wood pulps (DWP). The large variety of pulps was evaluated both applying commonly used and extraordinary quality parameters. The hypothesis of the study was that the variation within one group of generic dissolving pulps is higher than the variation between the different generic dissolving pulps. This hypothesis was confirmed for some parameters and, furthermore, recommendations for focus areas for possible process optimization were done.

The outcome of the benchmark study (4.1) fits well with the known background data and the corresponding technical and chemical differences of the wide variety of investigated pulps. Regarding the fiber morphology of DWP, a property which normally does not attract much attention, it could be concluded that both fiber length and fines content vary substantially within the generic pulps from hardwood (HW) and softwood (SW). This is interesting as dissolving wood pulp is classified by its raw material as HW- and SW-DWP, where SW is traded at a higher market price. The classification is done for technical reasons as SW with its longer and coarser fibers improves drainage from lye. The results of this study suggest that a sub-classification of HW and SW into pulps which favor, and disfavor, drainage could improve the optimal usage of the pulps. The time for drainage from lye can be directly determined with existing methods (Zellcheming Merkblatt III/13, version 1968 and Arbeitsblatt A III/1/72). This drainage behavior should be correlated to the more easily determined fiber morphology as measured with modern fiber measurement devices. It would also be of interest to find the correlation between fiber morphology, drainage from lye and drainage from water. Methods for the determination of drainability from water are simple standard methods frequently used for the characterization of paper pulp, water retention value (WRV) and drainability, e.g., according to Schopper Riegler (ISO 5267-1:1999). These easy-to-measure properties have the potential to contribute to the optimization of the pulp composition used.

Another conclusion from the benchmark study worth highlighting is the systematic difference between kraft and sulfite pulps destined for the same

application, namely the production of viscose staple fibers, with assumingly comparable resulting product quality. This study implies that sulfite dissolving pulps with an intrinsic viscosity of 420 – 560 ml/g, a polydispersity index (PDI) of > 4.5 and a R18 determined at 20 °C ( $R18/20$ ) < 95% correspond application-wise to kraft dissolving pulps with an intrinsic viscosity of 380 – 480 ml/g, a polydispersity index 3 - 4 and a  $R18/20$  > 95 %. The more uncommon analysis of R18 at 50 °C gave important information on the practical performance of a dissolving pulp. The results indicated that a lower R18 at 50° than at 20°C is mainly caused by more extensive xylan removal at the higher temperature level and depends on the initial hemicellulose content of the pulp. General expressions for the prediction of R18 at 50 °C ( $R18/50$ ) from the standard analysis  $R18/20$  were found. In the case of HW-pulps, which were shown to vary to a high extent regarding xylan content (2 – 6 %), the inclusion of the parameter xylan content improved the prediction considerably. This knowledge has the potential to improve the process control of the alkalization step.

The composition and the structure of the carbohydrates could be shown to have a strong influence on the result of the alkalization (4.2). For a specific dissolving pulp, a higher initial intrinsic viscosity was combined with a higher polydispersity index (PDI) and gave a higher absolute loss in intrinsic viscosity and PDI after alkalization and draining. A higher initial intrinsic viscosity also resulted in a higher resistance to alkaline extraction determined as  $R18/20$ . These findings indicate that the high-viscosity version of a pulp product - commonly chosen for higher product quality, due to the higher absolute intrinsic viscosity after processing – also improves process economy due to a lower process yield loss. To which extent reactivity would be affected was not addressed in this study. The contradicting parameters of process yield and purity were investigated in detail for three selected dissolving pulps by studying a wide span of different alkalization settings. It was found that different dissolving pulps followed the same general extraction behavior for chemical composition and carbohydrate structure when treated with aqueous alkali (10 - 18 wt% aq. NaOH at 20 – 50 °C). The results indicate that each dissolving pulp has different steeping settings that are optimal for the properties of the alkali cellulose or its regenerate. These properties are purity, yield, and degree of transformation to alkali cellulose. Extraction with 18 wt%

aq. NaOH gave for all dissolving pulps investigated optimal alkalization result regarding yield, purity, and transformation. The choice of steeping temperature was found to be important in order to balance the yield and the purity of xylan-containing pulps. One of the investigated pulps, a short-fiber kraft dissolving pulp with a somewhat elevated xylan content, showed the greatest variation in purity and a less pronounced transformation over the investigated range of alkali extractions. For this pulp, a narrower range of steeping settings that mirror today's viscose production conditions was investigated (17 - 20 wt% aq. NaOH at 40 – 50 °C). Conversion to alkali cellulose was shown to be uncritical within the applied range of settings. If high yield is top priority, alkalization at the lower temperature of the investigated range would be advantageous, giving a yield difference compared with the highest temperature of up to 1%-unit. At this low temperature, the lower alkali concentration would result in the highest extraction of xylan. Application of the lower process temperature and the lower alkali concentration would also be advantageous from an economical point of view. In practice, the required aging temperature for the needed rate of depolymerization might set the limit for the lowest possible alkalization temperature.

Dissolving pulps are usually dried prior to application, but there are also integrated processes using never-dried pulps. Never-dried pulps are supposed to deliver pulp with better processability due to less hornification of the pulp structure. It was, therefore, of relevance to investigate the structural changes induced by drying performed with differing severity as it might occur due to variations in the drying machine (4.3). The determination of the water retention value (WRV) gave the most consistent results. More sophisticated methods could support the findings. It could be concluded that possible process variations could result in a potential difference in hornification of 14 %. It would be interesting to determine the potential for improved processability by means of application studies.

The application study when carboxymethylating alkalized pulp from generic wood market pulps with extreme variation in hemicellulose content (1.5 – 22.8 wt%), intrinsic viscosity (391 – 780 ml/g), content of extractives (0.04 – 0.13 wt%) and content of cellulose II (maximum 33 %) found that favorable process

conditions with 15 wt% aq. NaOH turn all pulps used into well soluble carboxymethylated cellulose (CMC) with a high degree of substitution (DS 1.32 – 1.37), despite differences in the purity of the pulps (4.4). A DS of 0.64 – 0.77 was obtained when CMC was prepared in the presence of 5 wt% aq. NaOH. This DS was considered to be near the limit for water solubility of the CMC produced and gave the possibility to rank different pulps in terms of their solubility. It was shown that a high content of various impurities as found in a paper pulp interferes with the substitution reaction at the cellulose leading to lower solubility. Moreover, it was shown that the impurities downgraded the product properties by inhibiting thickening behavior even at high DS. A high degree of cellulose II as found in a high-purity DWP led to slightly impaired quality. However, the investigated cellulose-rich and cellulose-II-poor sulfite dissolving pulps (both HW and SW), had the best solubility. Even the xylan- and extractive-rich kraft DWP (HW) was found to be on the same level as the sulfite pulps in terms of solubility, while a more pure variant resulted in lower solubility. None of the various measured chemical and supramolecular properties could clearly explain these results which suggests further investigations on the reason for the different applicability of pulps.

Finally, the development of a non-destructive method to determine the degree of conversion to alkali cellulose as a result of alkalization requiring little time and material must be highlighted. The method is based on Raman spectroscopy and is a relative method where the treated material is compared to the initial material. The identified peaks and the logic of the calculation could be shown to deliver repeatable coherent results, even though the evaluation is relatively simple.

## **6 Zusammenfassung - Der Einfluss der Variation der Qualität des Zellstoffes auf die Alkalisierung**

Die globale jährliche Produktion von Chemiezellstoffen ist seit dem Jahr 2000 von drei Millionen auf acht Millionen Tonnen gestiegen. Die Verwendung der Zellstoffe für die Herstellung von Textilfasern aus Viskose und die steigende Nachfrage nach Textilien sind die Ursache für die Produktionssteigerungen. Chemiezellstoffe werden überwiegend aus Holz hergestellt und bestehen somit aus vereinzelt und modifizierten Holzfasern, in denen Zellulose der hauptsächliche Bestandteil ist. Im Zusammenhang mit dem Anstieg der Produktionskapazität haben viele neue Zellstoffprodukte den Markt betreten.

Diese Arbeit charakterisiert eine große Vielfalt von Marktzellstoffen. Die ausgewählten Zellstoffe sind vorwiegend für die Herstellung von Viskose vorgesehen. Es werden aber auch Papierzellstoffe und Chemiezellstoffe höherer Reinheit zum Vergleich herangezogen. Es wurde unter anderem gezeigt, dass die Faserlänge mehr variiert als die Standardcharakterisierung in Lang- und Kurzfasern impliziert und dass eine große Variation im Anteil von Feinstoffen zu erwarten ist. Diese Eigenschaften sind von prozesstechnologischer Bedeutung und sollten für eine optimale Applikation klassifiziert werden. Des Weiteren konnte herausgearbeitet werden, wie sich die generisch unterschiedlichen Zellstoffe hergestellt nach dem Sulfit- oder Kraftverfahren, angewandt in der selben Applikation, hinsichtlich ihrer Eigenschaften unterscheiden. Sulfitzellstoffe werden mit deutlich höherem mittlerem Polymerisationsgrad, einer höheren Polydispersität bezüglich der Molekulgewichtsverteilung und einer geringeren Resistenz gegenüber der Extraktion mit hochkonzentrierter Lauge (R18) als Kraftzellstoffe in identischen Applikationen eingesetzt.

Des Weiteren wurde das Verhalten ausgewählter Zellstoffe in der Alkalisierung, die die gewöhnlichste Vorbehandlung in der industriellen Verarbeitung, untersucht. Bei der Alkalisierung wird die Zellulose der Chemiezellstoffen zu Alkalizellulose umgewandelt. Es konnte gezeigt werden, dass der Xylangehalt die wichtigste Eigenschaft der Zellstoffe ist, und dass unterschiedliche Zellstoffe somit unterschiedliche optimale Prozesseinstellungen bezüglich Alkaligehalt und Temperatur vorweisen. Die zu optimierenden Eigenschaften der Alkalizellulose sind Ausbeute, Reinheit und Umwandlung

der Zellulose zu Natriumzellulose. Zur Bestimmung des Umwandlungsgrades wurde eine Methode unter Verwendung von Raman-Spektroskopie entwickelt. Extraktion bei ca. 18 wt% aq. NaOH, welche üblicherweise in der Industrie zur Anwendung kommt, zeigte sich für alle untersuchten Zellstoffe als vorteilhaft. Xylanärmere Zellstoffe waren unempfindlich bezüglich der resultierenden Ausbeute und Reinheit bei in der Industrie üblichen Extraktionstemperaturen zwischen 40-50 °C. Die Ausbeute des xylanreicheren Zellstoffes (3.7 %) war jedoch bei höherer Temperatur 1%-Einheit niedriger und die Reinheit gleichzeitig höher. Dieses Ergebnis beleuchtet das Potential einer gerichteten Prozessoptimierung bezüglich der verwendeten Zellstoffe und des gewünschten Produktionsresultates.

Markzellstoffe werden getrocknet gehandelt und es ist bekannt, dass die Trocknung, aufgrund ihres Einflusses auf die supramolekulare Struktur der Fasern, die Prozessbarkeit negativ beeinflusst. Die Änderungen der supramolekularen Struktur, die als Verhornung bezeichnet wird, konnten am besten mit Hilfe der Bestimmung des Wasserrückhaltevermögens quantifiziert werden. Unterschiedliche Trockenverfahren, die mögliche Prozessschwankungen einer Trockenmaschine simulieren, resultierten in Wasserrückhaltevermögen mit einer Differenz von 14 % zwischen dem höchsten und niedrigsten Wert und zeigen den Wert von Prozessverbesserungen bei der Zellstoffherstellung auf.

Da die Umwandlung zu Viskose im Labor komplex durchzuführen ist, wurden ausgewählte Zellstoffe in einer Applikationsstudie statt dessen zu CMC (carboxymethylierte Zellulose) umgesetzt. CMC ist ein weiterer bedeutungsvoller Applikationsbereich für Chemiezellstoffe, in dem ebenfalls die Alkalisierung als Vorbehandlung Anwendung findet. Es konnte gezeigt werden, dass lediglich extreme Gehalte von Verunreinigungen, wie sie in Papierzellstoffen vorliegen, zu stark verminderter Qualität des Produktes führen, wenn rationalisierte Synthesebedingungen zur Anwendung kommen. Chemiezellstoffe, hergestellt im Sulfitprozess, wiesen die beste Qualität auf. Qualitätsschwankungen, wie sie bei Dissolvingzellstoffen für die Eigenschaften Xylan- und Extraktgehalt auftreten, führten zu ähnlich guten Löslichkeiten. Der Umstand, dass festgestellte Qualitätsunterschiede zwischen den hergestellten

CMC nicht immer eindeutig mit den gemessenen chemischen und supra-molekularen Eigenschaften der Ausgangszellstoffe erklärt werden konnten, impliziert die Notwendigkeit weitere gerichtete Studien durchzuführen.



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## List of publications

### Publications in peer reviewed journals

1.

Influence of wood pulp quality on the structure of carboxymethyl cellulose

Fechter, Catharina; Heinze, Thomas

Journal of applied polymer science, 2019-09-10, Vol.136 (34), p.47862-n/a

2.

Influence of pulp characteristics on the properties of alkali cellulose

Fechter, Catharina; Fischer, Steffen; Reimann, Felix; Brelid, Harald;

Heinze, Thomas

Cellulose (London), 2020-08, Vol.27 (12), p.7227-7241

3.

Possibilities for Optimization of Industrial Alkaline Steeping of Wood-Based Cellulose Fibers

Fechter, Catharina; Brelid, Harald; Fischer, Steffen

Molecules (Basel, Switzerland), 2020-12-10, Vol.25 (24), p.5834

### Presentation at symposium

1.

Varför en dålig pappersmassa inte är en bra dissolvingmassa (Why is a bad paper pulp not a good dissolving pulp?)

Catharina Fechter

Ekmandagarna 2017, Stockholm Sweden

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## **Selbständigkeitserklärung**

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe..

Jena, 19.01.2022

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Catharina Fechter

## Appendix

**Table 12: Pulp sheet properties of different dissolving pulp samples**

<i>Sample</i> <sup>a</sup>	<i>Sheet dimensions, cm x cm</i>	<i>Bone dry grammage, g/m<sup>2</sup></i>
HWk 1a	83 x 70	x
HWk 1a-EX	n.d. <sup>b</sup>	902
HWk 2b	n.d.	1009
HWk 3b	80 x 63	811
HWk 4a	n.d.	752
HWk 4b	n.d.	793
HWk 5	n.d.	868
HWk 6	n.d.	764
HWk 7	78 x 60	755
HWk 8	83 x 70	938
HWk 9c	n.d.	823
HWk 10b	n.d.	934
HWk 11b	80 x 76	798
HWk 12b	80 x 63	827
HWs 1b	80 x 60	825
HWs 2a	74 x 71	1009
HWs 2b	n.d.	1058
SWs 1	X	x
SWs 2a	80 x 59	1198
SWs 2b	n.d.	1040
SWs 3b	n.d.	584
SWs 5	81 x 65	644
SWk 1a	n.d.	719
SWk 1b	n.d.	755
SWk 2	79 x 60	754
SWk-hp 1	69 x 52	x
SWk-hp 2	80 x 62	834
HWk-hp 1	n.d.	755
HWk-hp 2	80 x 63	837

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12) distinguishes different commercially available pulp products. a and b represent respective random sample from a pulp product. EX – variation of a standard product with elevated content of extractives and xylan

<sup>b</sup> n.d. – not determined

**Table 13: Fiber morphology of different market pulp samples**

<i>Sample<sup>a</sup></i>	<i>Fiber length, mm</i>	<i>Fiber width, <math>\mu</math>m</i>	<i>Fines, %</i>
HWk 1a	0.74	21.1	n.d. <sup>b</sup>
HWk 1a-ex	0.72	20.9	n.d.
HWk 1a-EX	0.73	19.8	3.4
HWk 1b	0.70	20.4	4.1
HWk 1c	0.70	20.4	3.9
HWk 2b	0.72	20.3	n.d.
HWk 3a	0.70	15.5	7.5
HWk 3b	0.74	16.6	6.4
HWk 4a	0.58	15.9	n.d.
HWk 4b	0.61	15.3	n.d.
HWk 5	0.70	16.7	6.1
HWk 6	0.63	14.9	7.1
HWk 7	0.69	16.0	7.7
HWk 8	0.59	15.5	13.2
HWk 9a	0.64	15.9	7.9
HWk 9b	0.67	16.4	7.8
HWk 9c	0.70	16.6	n.d.
HWk 10a	0.64	15.7	9.8
HWk 10b	0.70	16.0	n.d.
HWk 11a	0.85	18.1	2.9
HWk 11b	0.87	18.0	3.0
HWk 11c	0.80	18.8	3.7
HWk 12a	0.71	17.2	9.2
HWk 12b	0.65	16.6	9.0
HWs 1a	0.59	17.4	12.1
HWs 1b	0.60	17.6	12.4
HWs 2a	0.61	16.7	8.6
HWs 2b	0.61	17.7	n.d.
HWs 3	0.73	19.7	19.6
SWs 1	1.73	27.0	7.5
SWs 2a	1.77	26.4	11.2

Continue page XXI



Cont. Table 13

Sample <sup>a</sup>	Fiber length, mm	Fiber width, $\mu$ m	Fines, %
SWs 2b	1.73	26.0	9.5
SWs 3a	1.96	28.9	10.0
SWs 3b	1.96	28.7	10.3
SWs 4	1.74	26.3	6.8
SWs 5	1.62	28.8	7.0
SWk 1a	2.46	30.5	n.d.
SWk 1b	2.62	30.1	n.d.
SWk 2	1.97	30.1	4.8
SWk-hp 1	2.26	30.7	3.9
SWk-hp 2	2.18	29.1	2.9
HWk-hp 1	0.95	19.4	n.d.
HWk-hp 2	0.66	16.0	6.6
HWk-paper	0.93	21.5	8.4
SWk-paper	2.47	30.0	n.d.

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12) distinguishes different commercially available pulp products. a - c represent respective random sample from a pulp product. EX resp. ex – variation of a standard product with elevated content of extractives and xylan (ex < EX)

<sup>b</sup> n.d. – not determined

**Table 14: Carbohydrate composition of different pulp samples**

<i>Sample</i> <sup>a</sup>	<i>Viscosity,</i>  <i>ml/g</i>	<i>R18/20</i>  <i>%</i>	<i>R18/50</i>  <i>%</i>	<i>R10/20</i>  <i>%</i>	<i>Glukan</i>  <i>mg/g</i>	<i>Xylan</i>  <i>mg/g</i>	<i>Man- nan</i>  <i>mg/g</i>	<i>Kla- son lignin</i> <i>mg/g</i>	<i>Acid- soluble lignin</i> <i>mg/g</i>	<i>Acetone extract</i>  <i>%</i>
HWk 1a	412	96.3	94.7	92.5	956	34	5	0	4	0.04
HWk 1a-ex	391	96.9	95.3	93.4	954	37	4	0	4	0.09
HWk 1a-EX	440	96.3	94.3	92.3	944	45	6	1	4	0.13
HWk 1b	484	97.3	95.4	94.9	951	40	4	1	4	0.07
HWk 1c	376	96.7	95.2	92.9	955	37	5	0	4	0.08
HWk 2a	474	n.d. <sup>b</sup>	95.5	n.d.	952	39	4	0	4	0.05
HWk 2b	484	97.6	95.4	94.9	953	38	4	0	4	0.09
HWk 3a	417	96.7	96.5	93.4	970	21	2	0	5	0.09
HWk 3b	463	97.2	n.d.	92.4	964	30	2	0	4	n.d.
HWk 4a	434	96.3	95.8	n.d.	971	22	1	0	4	0.36
HWk 4b	435	95.7	93.6	92.3	943	49	2	0	5	0.38
HWk 5	402	96.2	94.3	91.8	954	40	2	0	4	0.10
HWk 6	444	96.8	96.3	94.5	967	27	2	0	4	0.09
HWk 7	421	96.9	95.3	93.2	963	30	2	0	4	0.05
HWk 8	400	96.6	96.5	91.0	973	19	2	0	4	0.01
HWk 9a	462	97.4	96.9	95.1	976	19	1	0	4	0.08
HWk 9b	408	97.7	97.0	94.5	975	18	1	0	5	0.13
HWk 9c	448	97.8	97.5	94.0	977	17	1	0	4	0.11
HWk 10a	421	96.9	96.6	93.1	974	20	2	0	4	0.13
HWk 10b	389	97.3	96.5	92.5	969	25	1	0	4	0.19
HWk 11a	519	95.3	n.d.	93.2	929	61	3	0	4	0.22
HWk 11b	412	95.6	n.d.	91.7	938	57	4	0	0	n.d.
HWk 11c	n.d.	95.2	n.d.	n.d.	943	53	4	n.d.	n.d.	0.02
HWk 12a	475	95.1	n.d.	90.9	938	51	6	0	4	0.23
HWk 12b	472	96.7	n.d.	93.1	957	37	5	0	0	n.d.
HWs 1a	516	95.2	94.8	91.0	968	23	3	1	5	0.23
HWs 1b	420	95.3	95.2	90.5	968	23	0	0	5	0.22
HWs 2a	585	93.5	92.6	89.3	950	34	9	0	6	0.22
HWs 2b	557	95.2	95.0	91.5	965	24	4	0	6	0.30
HWs 3	475	94.6	n.d.	87.2	962	24	6	0	3	0.22
SWs 1	560	94.4	94.3	90.1	960	14	21	0	4	0.12

Continue page XXIII

## Appendix

Cont. Table 14

Sample <sup>a</sup>	Viscosity, ml/g	R18/20 %	R18/50 %	R10/20 %	Glukan mg/g	Xylan mg/g	Man- nan mg/g	Kla- son lignin mg/g	Acid- solubl e lignin mg/g	Acetone extract %
SWs 2a	522	94.7	94.4	87.6	965	12	13	5	4	0.04
SWs 2b	457	95.1	95.0	88.7	969	14	13	0	3	0.15
SWs 3a	533	95.2	94.4	90.6	962	16	16	1	4	0.13
SWs 3b	555	94.6	n.d.	89.4	959	18	18	0	3	0.12
SWs 4	515	92.9	92.8	87.9	948	26	22	0	4	0.12
SWs 5	482	92.5	n.d.	86.6	953	18	23	1	5	0.28
SWk 1a	472	n.d.	95.1	n.d.	955	23	16	0	4	0.14
SWk 1b	448	96.1	95.5	92.8	955	23	16	0	4	0.29
SWk 2	366	95.9	n.d.	92.5	959	24	15	0	0	n.d.
SWk-hp 1	641	98.4	98.1	97.5	980	7	8	0	3	0.32
SWk-hp 2	595	97.8	n.d.	96.7	979	7	10	0	2	0.02
HWk-hp 1	700	n.d.	97.5	n.d.	982	10	4	0	3	0.02
HWk-hp 2	690	97.6	n.d.	96.5	974	16	2	2	5	0.24
HWk-paper	780	90.7	76.1	87.8	746	225	3	9	10	0.13
HWk-paper20	892	94.2	82.4	91.4	796	191	4	1	8	n.d.
HWk-paper14	930	95.6	87.8	93.0	854	135	4	1	7	n.d.
HWk-paper5	1022	n.d.	n.d.	n.d.	941	49	5	0	5	n.d.
SWk-paper	645	86.7	85.4	85.8	850	70	64	0	7	n.d.
SWk-paper11	669	90.1	89.0	89.3	878	44	66	0	6	n.d.
SWk-paper8	697	n.d.	n.d.	n.d.	915	20	57	0	5	n.d.

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12) distinguishes different commercially available pulp products; paper5-20 indicate the hemicellulose content in % after treatment of respective paper pulp according to Lund et al. (2012). a - c represent respective random sample from a pulp product. EX resp. ex – variation of a standard product with elevated content of extractives and xylan (ex < EX)

<sup>b</sup> n.d. – not determined

**Table 15: Molecular properties of different dissolving pulp samples**

<i>Sample</i> <sup>a</sup>	<i>Mn</i> , <i>kDa</i>	<i>Mw</i> , <i>kDa</i>	<i>Mz</i> , <i>kDa</i>	<i>Mw/Mn</i> ( <i>PDI</i> )	<i>DP</i> <50	<i>DP</i> <100	<i>DP</i> >2000	<i>DP</i> (162 Da /unit)
HWk 1a	54	172	356	3.2	1.7	4.3	14.2	1062
HWk 1a-ex	54	155	332	2.8	1.1	3.9	12.4	956
HWk 1a-EX	54	172	454	3.2	1.2	4.9	12.9	1062
HWk 1b	64	231	535	3.6	0.4	2	20.5	1428
HWk 1c	53	163	336	3.1	1.8	4.4	13.1	1004
HWk 2a	65	215	466	3.3	1.2	3.4	19.2	1327
HWk 3a	60	183	446	3.1	1.8	4.7	13.3	1132
HWk 4a	49	238	639	4.9	2	4.5	21.5	1471
HWk 5	57	173	377	3.1	1.9	5	13.3	1070
HWk 6	61	194	421	3.2	1.8	4.6	16.1	1198
HWk 9a	57	206	467	3.6	0.7	2.6	16.4	1269
HWk 9b	55	190	397	3.5	1.2	3.1	15.3	1175
HWk 9c	62	206	426	3.3	0.8	2.5	17.4	1270
HWk 10a	56	205	454	3.7	1.7	4.2	17.7	1265
HWk 10b	54	184	416	3.4	0.8	3.1	14.3	1136
HWk 11a	68	255	1108	3.8	1.6	5.4	21	1573
HWs 1a	39	229	611	5.9	2.2	5.5	20.7	1414
HWs 1b	53	234	671	4.4	1.9	5.1	20.8	1445
HWs 2a	47	288	824	6.2	3.8	8.5	26.5	1776
HWs 2b	58	307	924	5.3	1.9	4.9	28.2	1897
HWs 3	41	228	776	5.6	6.8	12.6	18.3	1407
SWs 1	45	284	832	6.4	3.2	7.3	25.8	1752
SWs 2a	60	257	666	4.3	2.4	5.5	23	1584
SWs 2b	51	244	725	4.8	2.4	5.2	21.6	1503
SWs 3a	37	250	691	6.7	3.1	6.1	22.6	1543
SWs 3b	48	316	1050	6.6	3.8	7.2	27.6	1953
SWs 4	35	303	923	8.8	3.8	8.1	26.4	1872
SWs 5	53	286	906	5.4	3.1	6.6	24.7	1763
SWk 1a	64	244	479	3.8	1.3	3.4	23.6	1503
SWk-hp 1	111	341	689	3.1	0.1	0.7	35.9	2104
SWk-hp 2	119	298	630	2.5	0	1.2	29.6	1836
HWk-hp 1	105	372	814	3.5	0.3	1.4	38.5	2293
HWk-paper	59	446	1394	7.6	0.5	4.1	37.9	2752

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12) distinguishes different commercially available pulp products. a - c represent respective random sample from a pulp product. EX resp. ex – variation of a standard product with elevated content of extractives and xylan (ex < EX)

**Table 16: Mineral matters of different dissolving pulp samples**

<i>Sample</i> <sup>a</sup>	<i>Ash, %</i>	<i>Si, ppm</i>	<i>Ca, ppm</i>	<i>Mg, ppm</i>	<i>Fe, ppm</i>	<i>Mn, ppm</i>	<i>Cu, ppm</i>
HWk 1a	n.d. <sup>b</sup>	3	41	53	< 1.0	< 0.5	< 0.5
HWk 1a-ex	0.04	4	43	63	1	< 0.5	< 0.5
HWk 1a-EX	0.06	<5	33	49	1.3	0.1	0.2
HWk 1b	0.04	3	33	57	1.5	<0.5	<0.5
HWk 1c	0.02	4	28	23	0.6	<0.2	0.1
HWk 2b	0.06	0	14	9	0.6	0.03	0.06
HWk 3a	0.1	<20	33	11	1.3	0.1	<0.1
HWk 3b	0.04	7	10	8	3.1	<0.1	<0.1
HWk 4a	0.04	40	18	5	13	n.d.	n.d.
HWk 4b	0.09	56	16	6	73.8	0.1	0.2
HWk 5	n.d.	39	8	2	4.3	0.3	<0.1
HWk 6	0.04	7	52	10	1.7	0.4	<0.1
HWk 7	0.07	67	43	13	10.6	0.6	<0.1
HWk 8	0.15	51	103	26	9.8	2	0.1
HWk 9a	0.05	11	56	20	2.2	<0.5	<0.5
HWk 9b	0.1	38	130	38	8.3	0.6	<0.1
HWk 9c	0.06	11	70	18	3.4	0.2	0.2
HWk 10a	0.02	31	26	14	7.7	<0.2	0.2
HWk 10b	0.05	7	48	26	6	<0.2	0.1
HWk 11a	0.14	n.d.	35	10	1	0.2	<0.1
HWk 11b	0.16	7	34	12	1.9	0.2	<0.1
HWk 11c	n.d.	n.d.	36	12	n.d.	n.d.	n.d.
HWk 12a	0.03	32	54	8	4.4	0.4	0.1
HWk 12b	0.07	20	100	14	2.2	0.4	0.2
HWs 1a	0.06	18	7	4	1.5	<0.5	<0.5
HWs 1b	0.1	5	16	2	1	<0.2	0.3
HWs 2a	0.08	n.d.	140	n.d.	0.7	0.3	<0.1
HWs 2b	0.09	14	96	21	1.7	<0.2	0.2
HWs 3	0.06	n.d.	25	7	0.7	<0.1	0.1
SWs 1	0.08	20	25	243	< 1.0	<0.5	<0.5
SWs 2a	0.04	34	15	n.d.	0.7	<0.1	<0.1
SWs 2b	0.1	5	10	4	0.8	<0.2	0.2
SWs 3a	0.07	15	12	38	< 1.0	<0.5	<0.5
SWs 3b	0.11	6	14	43	0.6	<0.1	<0.1
SWs 4	0.01	12	47	12	1.9	0.3	0.1
SWs 5	0.05	60	357	n.d.	7.8	0.5	0.2
SWk 1a	0.1	7	75	25	1	n.d.	n.d.
SWk 1b	0.15	4	46	15	0.8	0	0.1
SWk 2	0.13	2	24	10	0.5	<0.1	<0.1
SWk-hp 1	0.1	6	39	6	1	0.5	0.5
SWk-hp 2	0.1	n.d.	31	14	1.2	<0.1	<0.1
HWk-hp 1	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HWk-hp 2	0.08	n.d.	16	16	1.8	<0.1	<0.1
HWk-paper	0.62	682	379	725	37	1	< 0.5

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-12) distinguishes different commercially available pulp products. a - c represent respective random sample from a pulp product. EX resp. ex – variation of a standard product with elevated content of extractives and xylan (ex < EX)

<sup>b</sup> n.d. – not determined

**Table 17: Structural properties of eight different market pulps measured with CP/MAS <sup>13</sup>C-NMR spectroscopy, X-ray scattering (WAXS) and NIR FT Raman spectroscopy. Crystallinity index (CI), content of cellulose I (Cell I), content of cellulose II (Cell II) and content of amorphous cellulose (Ca) are given in % of total mass.**

a	WAXS						NMR				Raman		
	CI, %	Cell I, %	Cell II, %	width, nm	height, nm	length, nm	CI, %	Cell I, %	Cell II, %	LFD <sup>c</sup> , nm	Ca, %	Cell I, %	Cell II, %
HWk 1a	69	66	3	4.1	3.9	5.4	56	55	3	5.2	52	45	3
HWk 1a-ex	67	60	7	4.9	4.7	5.5	53	51	6	5.5	52	42	6
HWk 1a-EX	66	63	3	3.4	4.2	5.6	52	52	5	4.8	52	43	5
HWk 3a	58	58	0	3.9	5.0	4.6	55	56	-1	4.7	52	47	1
HWs 1a	67	64	3	3.6	4.8	5.3	53	53	2	4.5	53	44	3
SWs 1	70	67	4	4.3	4.6	5.7	56	54	1	4.6	54	43	3
SWk-hp 1	50	18	33	4.5/5.4 <sup>b</sup>	5.6/4.6	6.3/6.3	54	26	49	ind. <sup>d</sup>	47	25	28
HWk-paper	62	65	-3	3.3	4.5	5.6	41	48	6	ind.	53	43	4

<sup>a</sup> SW – softwood, HW – hardwood, s – sulfite, k – kraft, hp – high purity. The number (1-3) distinguishes different commercially available pulp products. a represents the respective random samples from a pulp product. EX resp. ex – variation of a standard product with elevated content of extractives and xylan (ex < EX)

<sup>b</sup> dimension of respective phase (Cell I and Cell II). The two results are based on resolvable reflexes of the respective phase.

<sup>c</sup> LFD – lateral fibril diameter

<sup>d</sup> ind. – indeterminable, no definite deconvolution possible

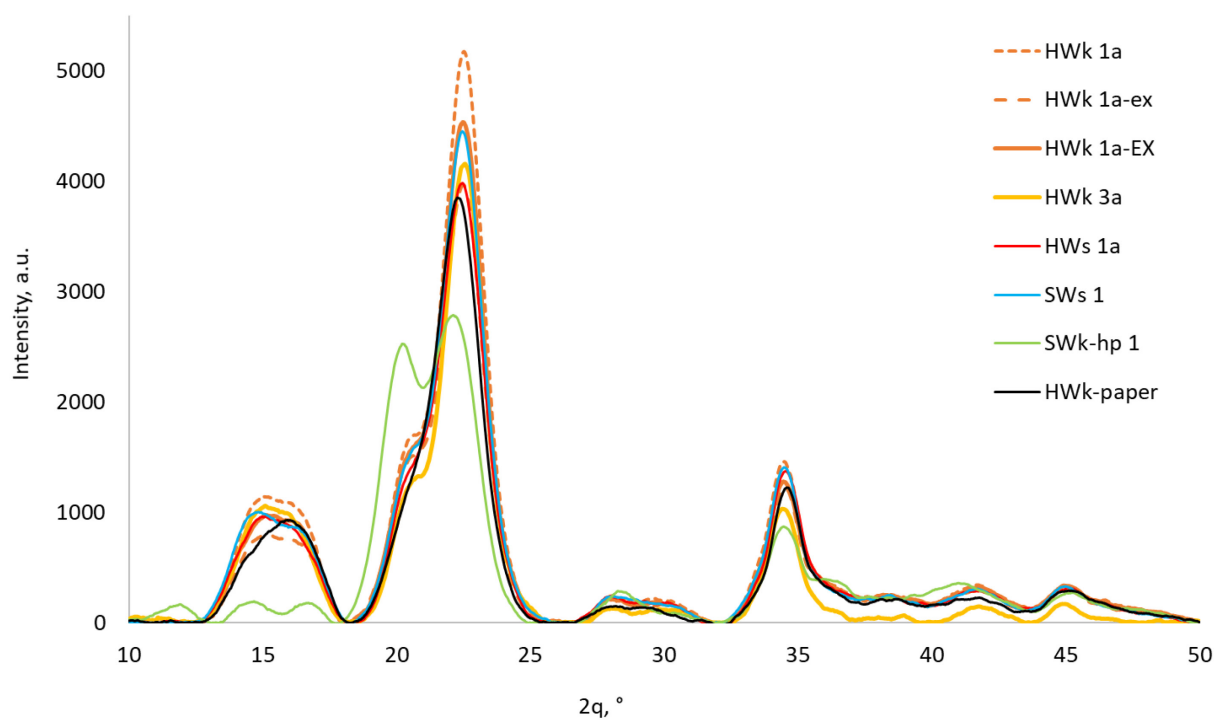


Figure 51: Scattering pattern from WAXS as intensity versus scattering angle of eight different market pulps

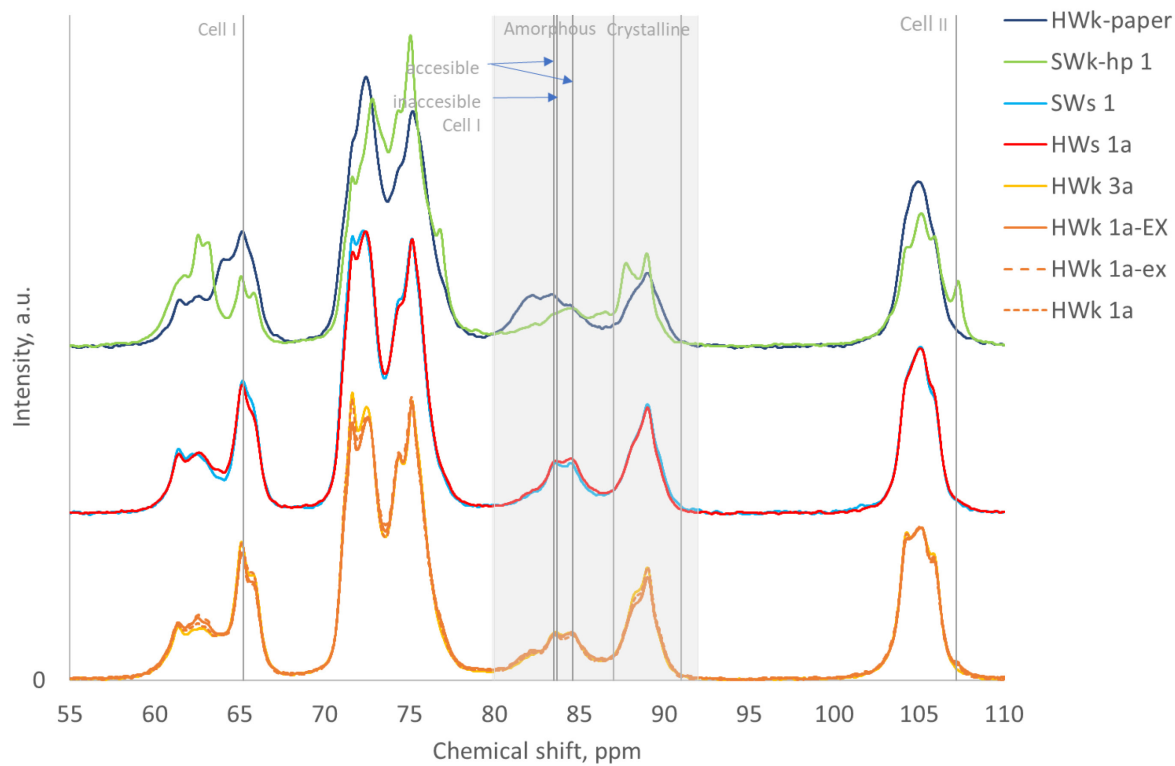
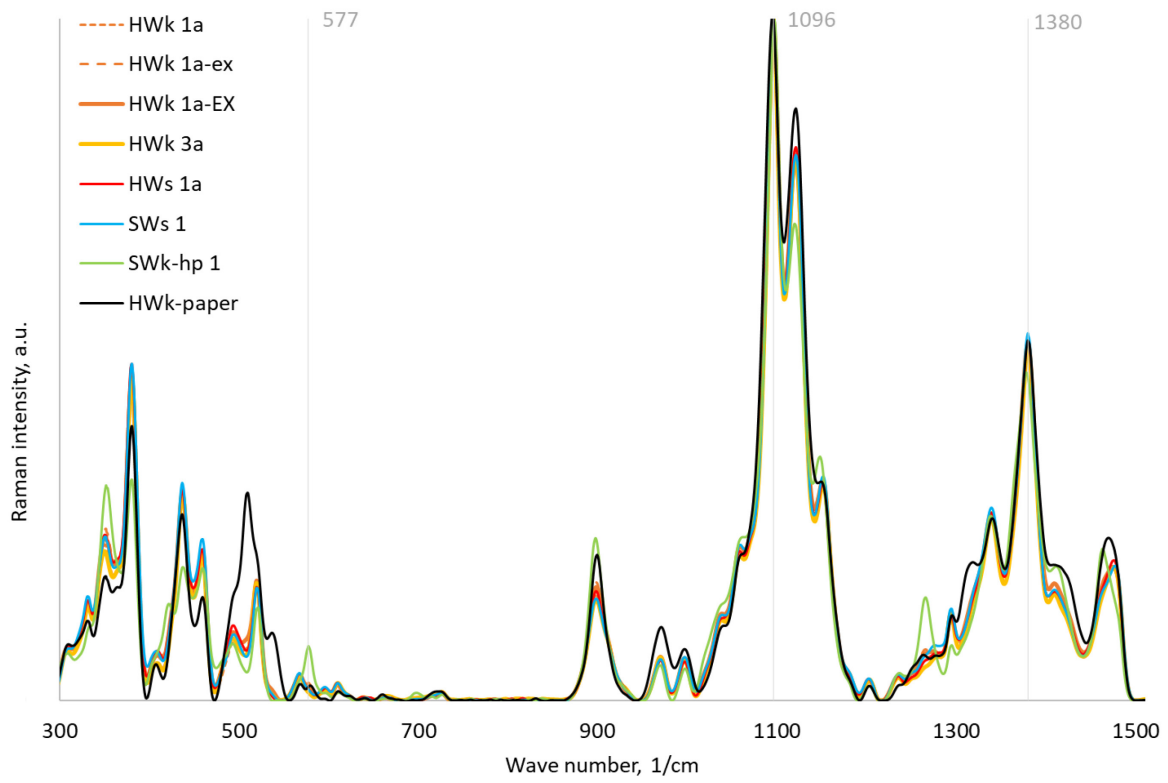


Figure 52: CP/MAS  $^{13}\text{C}$ -NMR spectra of eight different market pulps



**Figure 53: Raman-spectrum of eight different market pulps**



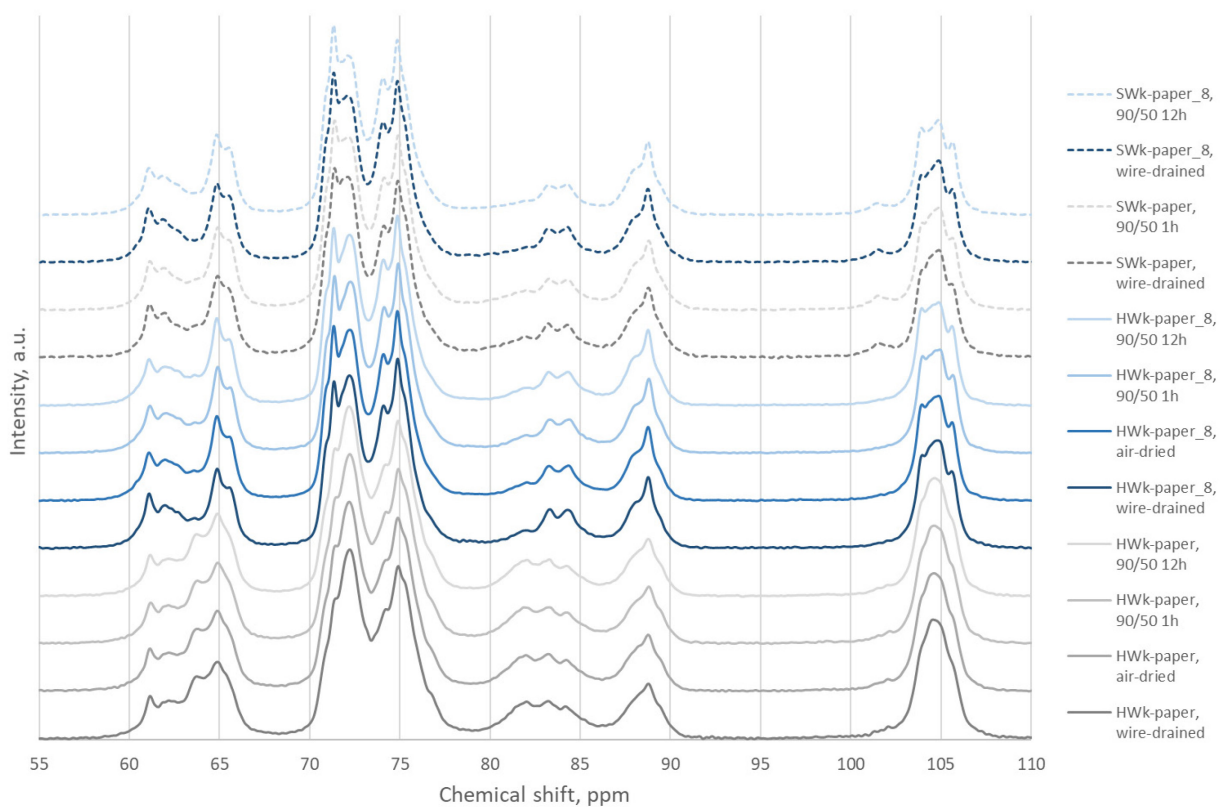
**Table 18: Structural properties of cold alkali extracted paper pulps dewatered according to four different procedures**

<i>a</i>	CP/MAS 13C-NMR								FSP		Pore		WRV
	<i>CI</i> <sup>b</sup> %	<i>Cell II</i> <sup>b</sup> , %	<i>LFD</i> nm	<i>s</i> <sup>c</sup>	<i>LFAD</i> nm	<i>s</i>	<i>SSA</i> <sub>LFAD</sub> m <sup>2</sup> /g	<i>s</i>	<i>g/g</i>	<i>s</i>	<i>size</i> nm	<i>s</i>	<i>g/g</i>
<b>HWK-paper</b>													
wet	41.3	6.6	3.9	0.1	47.2	7.5	57	9	1.44	0.13	51.0	9.3	1.60
air-dried	42.1	4.1	4.0	0.1	43.4	6.2	61	9	0.94	0.08	30.7	5.1	1.16
90/50 1h	42.3	6.1	4.0	0.1	48.6	7.3	55	8	0.99	0.10	36.0	6.4	1.03
90/50 12h	42.5	5.0	4.1	0.1	46.7	7.8	57	9	0.70	0.13	24.5	6.1	1.00
<b>HWK-p.._8</b>													
wet	48.4	2.6	3.8	0.1	20.3	0.8	131	5	1.57	0.06	24.0	1.4	1.62
air dried	50.2	1.7	4.0	0.1	23.9	1.2	112	5	1.00	0.13	17.9	2.5	0.94
90/50 1h	51.0	2.2	4.2	0.1	25.8	1.7	103	7	0.62	0.14	12.0	2.9	0.84
90/50 12h	51.2	1.5	4.2	0.1	26.3	1.5	101	6	0.69	0.01	13.6	0.8	0.82
<b>SWk-paper</b>													
wet	50.3	1.0	4.5	0.1	29.8	2.3	89	7	1.27	0.27	28.3	6.5	1.36
90/50 12h	51.1	2.6	4.7	0.1	30.6	2.4	87	7	0.78	0.09	17.8	2.5	0.86
<b>SWk-p.._8</b>													
wet	51.5	1.9	4.4	0.1	20.9	1	127	6	1.24	0.07	19.5	1.5	1.34
90/50 12h	53.2	1.1	4.8	0.1	23.8	1.6	112	7	0.78	0.08	14.0	1.7	0.76

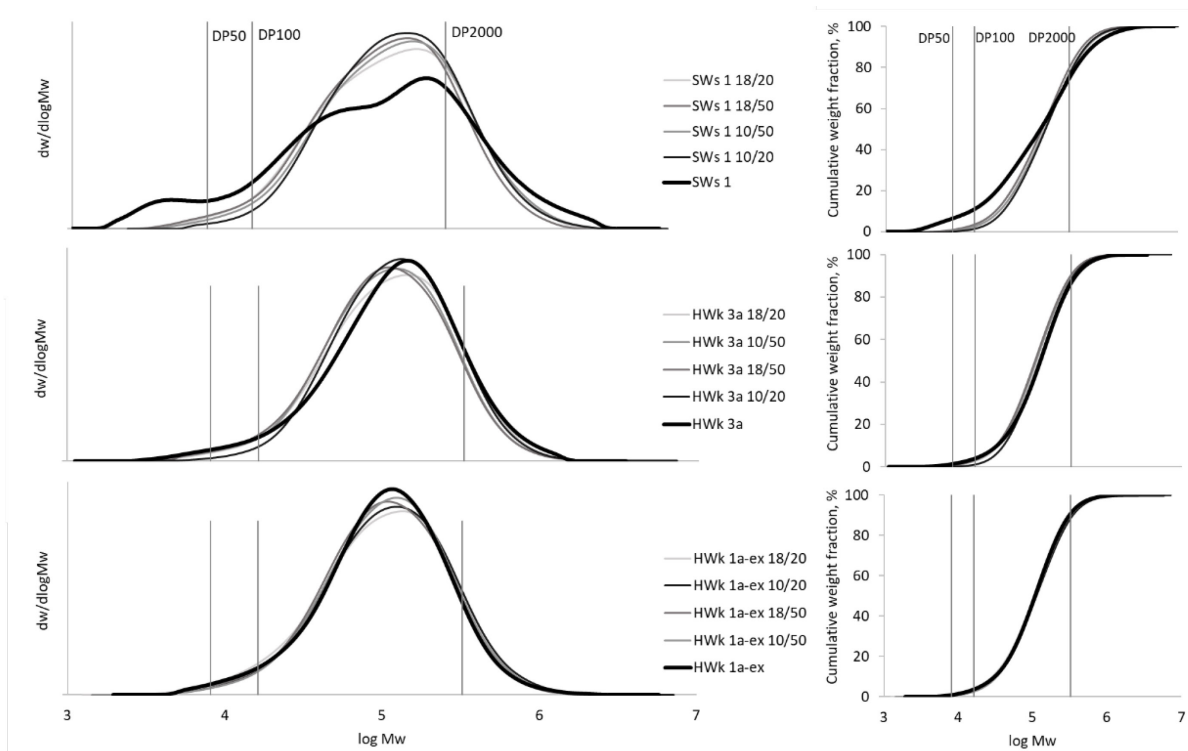
<sup>a</sup> HW – hardwood, SW – softwood, k – kraft, 8 - concentration of aq. NaOH in wt% used for cold alkali extraction of the starting pulp

<sup>b</sup> Crystallinity index (CI) and content of cellulose II (Cell II) are given in % of total dry sample mass

<sup>c</sup> standard deviation in respective unit



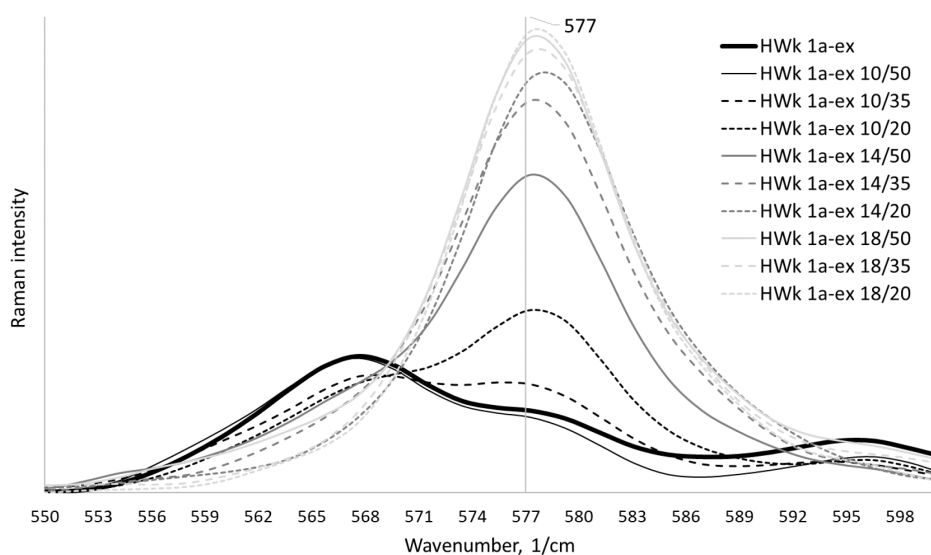
**Figure 54: CP/MAS  $^{13}\text{C}$ -NMR spectra of cold alkali extracted paper pulps dewatered according to four different procedures**



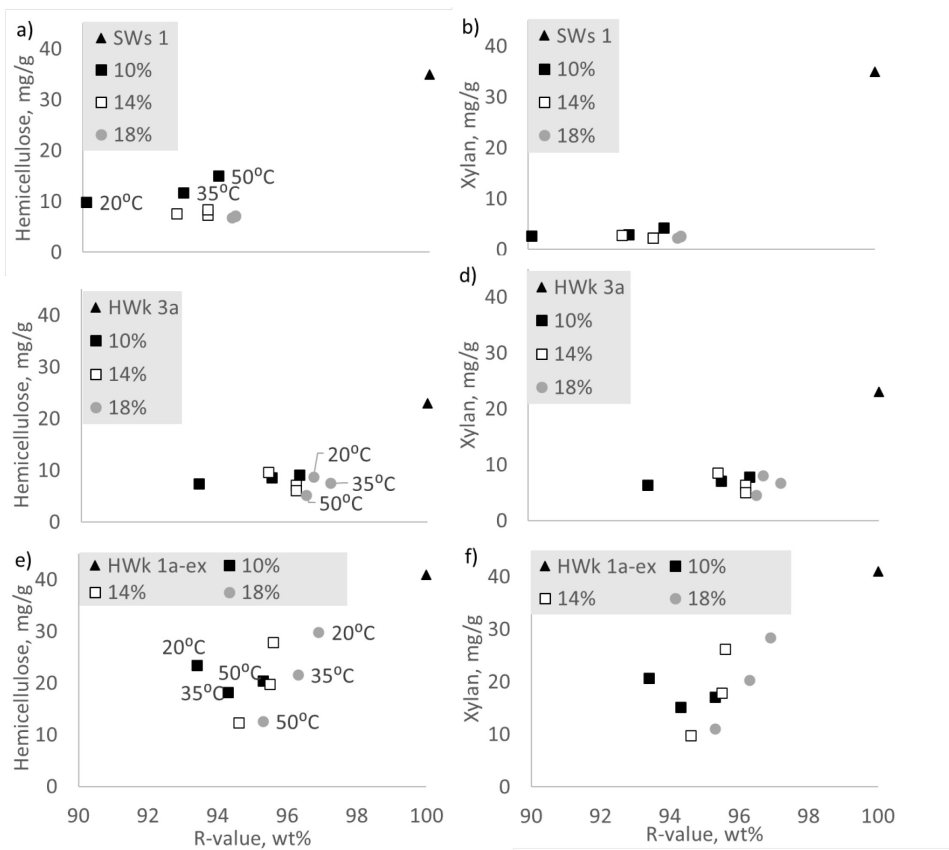
**Figure 55: Molecular weight distribution of pulps (SW - softwood, HW - hardwood, s - sulfite, k - kraft, ex - high xylan) and their regenerate after alkalization at different concentrations and temperatures (concentration of aqueous NaOH 10 or 18 wt%; temperature 20 or 50 °C).**

**Left: Absolute frequency distribution.**

**Right: Cumulative frequency distribution.**



**Figure 56: Raman-intensities at a small selection of wavenumbers for short-fiber kraft pulp (HWk 1a-ex) and its alkalinized residues. Alkalization was done with 10, 14, or 18 wt% aq. NaOH at 20, 30, or 50 °C, respectively.**



**Figure 57: Relationship of yield and hemicellulose content in residue after alkali extraction. Alkalization was done with 10, 14, or 18 wt% aq. NaOH at 20, 30, or 50 °C, respectively. a+b) SWs 1 – softwood sulfite pulp; c+d) HWk 3a – hardwood kraft pulp; e+f) HWk 1a-ex – hardwood kraft pulp with high xylan**