Influence of pulp characteristics on the properties of alkali cellulose

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Abstract Alkali extraction of cellulose material is a common treatment for several industrial processes—especially the viscose process, which produces fibers for textile applications. This study investigated different generic dissolving wood pulps by means of alkali extraction (10–18 wt% aq. NaOH at 20–50 °C). The regenerated residue of the pulps was characterized for its chemical composition, molecular structure, and cellulose conformation. The investigated pulps had in common that glucan was most intensely extracted at low temperature and low concentration of aqueous alkali, xylan was most intensely extracted at high temperature and high concentration of aqueous alkali, and mannan was most intensely extracted at a concentration of aqueous alkali > 14 wtwt% at all temperatures applied. The degree of transformation via alkali cellulose to cellulose II as determined with

Raman spectroscopy was found to be maximized for all pulps at high alkali concentration and temperature had no major influence. Maximum yield for all investigated pulps was found when extraction was done with 18 wt% aq. NaOH. The importance of temperature differed for the investigated pulps. The reason for the differences in extraction behavior or different absolute levels of resulting properties was found to be related to differences in the homogeneity and purity of the pulps. A conclusion of interest for industrial applications was that extracting the pulps with 18 wt% aq. NaOH led to an optimal alkalization result for yield, purity, and conversion. The steeping temperature chosen was found to be important to balance the yield and the purity of xylan-containing pulps.

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Graphic abstract

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Introduction

The demand for viscose fibers is increasing because of the increase in world population, prosperity as well as demand for fashion and other related consumer products. More than 90% of today's seven million tons of viscose fiber are produced using dissolving pulp derived from wood (DWP). Accordingly, this increasing demand is met by an extension of global DWP capacity. This capacity has almost doubled from 2008 to 2018 (Young 2018).

The first process step in producing viscose is the alkalization (steeping) and subsequent pressing of the pulp (Götze 1967). This treatment turns the pulp thoroughly into highly swollen alkali cellulose (Na-Cell). Na-Cell is able to react with carbon disulphide in the subsequent xanthation step. Moreover, Na-Cell is easy to depolymerize by means of the oxidation that occurs 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. 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.

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 and transforming the cellulose part into Na-Cell, two things happen: swelling of the entire solid polymer structure; and the dissolution of polymers with a low DP, i.e. hemicelluloses and low-molecular fractions of the cellulose. The intensity of these processes depends on the temperature and alkali concentration applied.

Cellulose is a heterogeneously structured polymer consisting of a mixture of low-ordered amorphous regions and highly-ordered crystalline regions. The amorphous regions are easily accessible when dispersed and swell in any polar solvent. This is not the case for crystalline regions. The amount of crystalline parts, indicated by the crystallinity index (CI), depends on the origin and pretreatments of the cellulose. Typical values for the CI of wood pulps determined with X-ray are 50–60% (Sixta 2006b). Given the fact that reactions with cellulose take place at the hydroxyl groups at Position 2, 3 and 6, it is obvious that a high CI will decrease the reactivity as the amount of available hydroxyl groups becomes

considerably lower. However, intracrystalline swelling of the structure in an alkaline medium converts crystalline cellulose into Na-Cell and breaks hydrogen bonds in the cellulose structure. This process makes the hydroxyl groups accessible for subsequent chemical 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 gives information on the resistance of a specific pulp to alkalization. Nevertheless, Fink et al. (1982) have 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. 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.

At room temperature, intercrystalline swelling, i.e. filling the pores between the crystallites, 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%. 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, H₂O and the Na⁺OH⁻ 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).

Swelling upon alkali treatment favors the dissolution of polymers in the pulp. The dissolved polymers, i.e. hemicelluloses and short-chained cellulose, can be removed easily by pressing. 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 fragmentation reactions have been shown to appear at temperature levels ≥ 40 °C in combination with high alkali concentration of around 18 wt% aq. NaOH (Mozdyniewicz et al. 2014; Sixta et al. 2004). Fragmentation will create additional alkali-soluble substance, which decreases the process yield.

Regarding the viscose process, the optimal choice of steeping 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 through pressing, and the processability of both lye and 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 sulphite 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 s. 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 and Sihtola 1963; Sihtola and Nizovsky 1963), but even the application of today's slurry alkalization has occurred in the past (Treiber et al. 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. 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. The need to understand the optimization strategy of the industrial steeping process has been identified, and an approach is provided in the present study.

The aim of this study is to elaborate possibilities for the optimization of the alkalization step within the viscose process. Generic pulps and their different regenerated alkali cellulose (rAC) are described in detail in terms of their chemical composition and structure properties. The steeping settings applied reflect 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).

Experimental

Materials

Six genetically different pulps were studied (Table 1). Two long-fiber pulps, originating from softwood, were selected: a sulphite pulp (*LFs*) that is used in the

production of standard viscose staple fibers (VSF); and a highly pure long-fiber kraft pulp (*LFk-hp*) that is applied in the production of cellulose derivatives. Short-fiber pulps, originating from hardwood, were represented with a sulphite (*SFs*) and two kraft pulps (*SFk*, *SFk-x*) used in VSF production, as well as a paper-grade kraft pulp (*SFk-paper*). *SFk-x* 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). The residue (R) obtained using the procedure was considered as rAC.

Acetic acid 95–97%, aq. NaOH p.a., water-free sodium acetate (CH_3COONa) 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, dihydrocholesterol (5α -cholestane- 3β -ol), 13-methylpentadecanoic acid (anteiso-C16:0), pyridine, HNO_3 p.a., HCl p.a., La_2O_3 p.a., CsCl p.a., copper ethylene-diamine solution (1.00 mol/l), LiCl, and N,N-dimethylacetamide, 99.9 + %, were purchased from Sigma Aldrich (Sweden).

Methods

Analysis of alkali resistance of pulps and the production of alkali cellulose

Alkali resistance (ISO 699:2015) of the pulps was determined as the R-value, and residues for further investigations were produced with 10, 14 and 18 wt% aq. NaOH at 20, 35 and 50 °C according to the

Table 1 Fiber type, raw material, and production process of the pulps used in this study (Pöyry Management Consulting Oy 2017)

Sample ^a	Fiber type	Raw material	Process ^b
LFk-hp	Long fiber	Pine	Kraft—Chlorine bleached
LFs	Long fiber	Pine/spruce	Sulphite—TCF
SFs	Short fiber	Eucalyptus (Dunii/Grandis)	Sulphite—ECF
SFk	Short fiber	Eucalypts (Urophylla)	Kraft—ECF
SFk-x	Short fiber	Birch/aspen	Kraft—ECF
SFk-paper	Short fiber	Birch/aspen	Kraft—TCF

^aLF, long fiber; SF, short fiber; s, sulphite; k, kraft; hp, high purity; x, high xylan

^bTCF, totally chlorine-free bleached; ECF, elemental chlorine-free bleached

scheme given in Table 2. No further modifications from the standard procedure, ISO 699:2015, had to be considered when the alkali concentration was altered. When applying temperatures $> 30\text{ }^{\circ}\text{C}$, a finer glass filter (40–100 μm) had to be used to compensate for the lower viscosity of the liquid. The residue (R) was regenerated alkali cellulose (rAC) and was used for further investigations.

Analysis of pulps and regenerated alkali cellulose (rAC)

The carbohydrate composition was analyzed via acid hydrolysis (TAPPI—T 249 cm-85) using 72 wt% aq. H_2SO_4 . 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 $113\text{ dm}^3\text{ g}^{-1}\text{ cm}^{-1}$ for hardwood pulps and $128\text{ dm}^3\text{ g}^{-1}\text{ cm}^{-1}$ 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.

Intrinsic viscosity (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 μm , $7.5 \times 300\text{ mm}$) from Agilent. Data processing was done in Astra6 to calculate key values such as the weight-average degree of polymerization (DPw, DP), the polydispersity index (PDI), and the weight fraction of molecules with $\text{DP} < 100$.

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. 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 analyzed using OPUS software. All spectra of one sample were combined into one, and this averaged spectrum was then handled with OriginPro. Amorphous cellulose, cellulose I and cellulose II were calculated according to Schenzel et al. (2005), Schenzel et al. (2009) and Agarwal (2017).

Table 2 Preparation of residues from pulp samples as regenerated alkali cellulose for further investigations, x

Sample ^a	R10/20	R10/35	R10/50	R14/20	R14/35	R14/50	R18/20	R18/35	R18/50 ^b
LFk-hp	(x)						(x)		x
LFs	x	x	x	x	x	x	x	x	x
SFs	(x)						(x)		x
SFk	x	x	x	x	x	x	x	x	x
SFk-x	x	x	x	x	x	x	x	x	x
SFk-paper	(x)						(x)		x

(x) only determination of alkali resistance; cf. Table 1 for the denotation of the samples

^aLF, long fiber; SF, short fiber; s, sulphite; k, kraft; hp, high purity; x, high xylan

^bR, residue after alkali extraction; 10, 14 resp. 18, concentration in wt% aq. NaOH used for alkali extraction; 20, 35 resp. 50, temperature in $^{\circ}\text{C}$ used for alkali extraction

Results and discussion

Change in chemical composition of pulp caused by alkalization

The pulps investigated contained a wide variety of hemicellulose (Table 3). The lowest mannan content was found in the short-fiber pulps *SFs*, *SFk*, *SFk-x* and *SFk-paper*. These pulps had three different levels of xylan content, and two of them were investigated in detail for different alkalization settings (*SFk* and *SFk-x*, Table 2). The long-fiber pulps possessed two mannan levels. The pulp with the highest hemicellulose content was chosen for detailed investigation (*LFs*). The high level of cellulose II (Cell II) in *LFk-hp* was supposed to be connected to the high purity level with regard to hemicellulose, which often demands an alkaline purification step in the fiber line. In a

comparison of dissolving pulp qualities, the polydispersity index PDI for the sulphite pulps was found to be significantly higher than that for the kraft pulps, resulting in generally low levels of R-values for the sulphite pulps. This is according to literature (Sixta 2006b). *SFk-paper* had an even higher PDI, which can be explained by the high level of xylan.

Considering the residue after alkaline treatment, *LFs*, *SFk*, and *SFk-x* showed the same extraction behavior when treated with aq. NaOH (Fig. 1). 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

Table 3 Properties of the investigated pulps

Sample ^a		LFk-hp	LFs	SFs	SFk	SFk-x	SFk-paper
<i>Chemical composition^b</i>							
Glucan	mg g ⁻¹	980	960	968	970	954	746
Xylan	mg g ⁻¹	7	14	23	21	37	225
Mannan	mg g ⁻¹	8	21	3	2	4	3
Klason lignin	mg g ⁻¹	0	0	1	0	0	9
Acid-soluble lignin	mg g ⁻¹	3	4	5	5	4	10
<i>Molecular structure</i>							
Intrinsic viscosity	ml g ⁻¹	641	560	516	417	391	780
DPw (SEC) ^c		2104	1752	1414	1132	1048	2752
PDI ^d		3.1	6.4	5.9	3.1	2.8	7.6
C _a (Raman ^e)	%	47	54	53	52	52	53
Cell I (Raman)	%	25	43	44	47	43	43
Cell II (Raman)	%	28	3	3	1	5	4
<i>Alkali resistance</i>							
R10/20 ^f	wt%	97.5	90.1	91.0	93.4	93.4	87.8
R18/20	wt%	98.4	94.4	95.2	96.7	96.9	90.7
R18/50	wt%	98.1	94.3	94.8	96.5	95.3	76.1
R18/20–R18/50	wt%	0.3	0.1	0.4	0.2	1.6	14.6

^aLF, long fiber; SF, short fiber; s, sulphite; k, kraft; hp, high purity; x, high xylan

^bSaccharides are reported as pure anhydrous polysaccharides. Ash content is not reported

^cWeight average degree of polymerization determined with size-exclusion chromatography

^dPolydispersity index determined with size-exclusion chromatography

^eParameter of cellulose structure measured with Raman spectroscopy and evaluated according to Agarwal (2017) as a fraction of total cellulose. C_a, amorphous cellulose; Cell I, cellulose I; Cell II, cellulose II

^fR, R-value as residue after alkaline extraction; 10 or 18, wt% aq. NaOH used for extraction; 20 or 50, extraction temperature in °C

Fig. 1 Residue, expressed as R-value upon extraction of pulp with aqueous NaOH at different concentrations and temperatures. LF—long fiber, SF—short fiber, s—sulphite, k—kraft, x—high xylan

1989). 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 *LFs*, *SFk*, and *SFk-x* 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. *SFk-x* changed already at 14 wt% aq. NaOH to decreasing R-value, *SFk* at 18 wt%, and *LFs* remained constant even at the highest alkali concentration applied. *LFs* showed the absolute maximum of R-value at 18 wt% aq. NaOH at any temperature applied. *SFk* reached a maximum R-value at 18 wt% and 35 °C, and *SFk-x* at 18 wt% and 20 °C.

It was found that less xylan was extracted from *SFk-x* at 20 and 35 °C when the alkali concentration was increased, which corresponds to the increase in

R-value at the same settings (Fig. 2a–c). 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 concentration and a high temperature. *SFk*, which contained less xylan than *SFk-x*, showed the same behavior but less pronounced. Extracting *LFs*, 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 *LFs*, *SFk*, and *SFk-x* 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 sulphite pulp upon extraction with aqueous alkali at different temperatures. The key properties of this pulp were found to be equal to the *SFk-x* of the present study (R18 93.4%; 4.0% xylan). Those authors have found that xylan removal has been

Fig. 2 a–c Loss of carbohydrates in the residue after extraction of pulp with aqueous NaOH at different concentrations and temperatures. **a** SFk-x—short-fiber kraft pulp with high xylan; **b** SFk—short-fiber kraft pulp; **c** LF—long-fiber sulphite pulp

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 (Fig. 3), which highlights that a higher temperature (50 °C) results in even higher levels of xylan extraction when the alkali concentration is increased from 10 to 14 and 18 wt% aq. NaOH. *LFs*, *SFk* and *SFk-x* seemed to have different extraction optima, however, that was not possible to be exactly determined in this study. *SFk-x*, with the highest initial xylan content, illustrated the process of xylan removal upon alkalization within the investigated settings in

Fig. 3 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). LF—long fiber, SF—short fiber, s—sulphite, k—kraft, x—high xylan. 20, 35 resp. 50—temperature in °C used for alkali extraction

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. *SFk* and *LFs* are assumed to develop in the same way but to a less pronounced extent.

The study considered an even wider variety of pulps by applying a minimized trial scheme (Table 3). This trial scheme included the standard extraction settings for the evaluation of dissolving pulp, R18 and R10 at 20 °C (R18/20 and R10/20), and R18 at 50 °C (R18/50), as this setting was seen to be relevant for today's production of viscose staple fiber. The higher amount of extracted material from the pulp indicated by the lower R-value due to extraction at a low alkali concentration (R10/20) or a higher temperature and a high alkali concentration (R18/50) was confirmed for all pulps investigated (Table 3). The difference between R10/20 and R18/20 is considered to be related to PDI, where a large difference indicates a wide PDI (Sixta 2006b). The present study could not clearly show this relationship, which might be due to the different viscosity levels and process histories of the investigated pulps. Nevertheless, the effect of high temperature combined with a high alkali concentration on the decrease of residue, in comparison to extraction at low temperature (R18/50:R18/20), was correlated to the hemicellulose content present in the pulp (Table 3). This was found for short-fiber pulps, in particular.

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 Fig. 2). 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” (Fig. 6) 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

sulphite 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 (Fig. 2).

The extraction of substance of low-molecular mass is supposed to decrease PDI. This became obvious for *LFs*, in which PDI decreased from 6.4 in the raw material to below 4.0 in the extracted samples. PDI in *SFk* decreased, to a lesser extent, from 3.1 to significantly below 3.0. The minor decrease in PDI of *SFk-x*, 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, Fig. 1) 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.

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” (Fig. 6)

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

^aLF, long fiber; SF, short fiber; s, sulphite; k, kraft; x, high xylan; xx/yy, 10 or 18 wt% aq. NaOH, 20 or 50 °C used for extraction

^bPolydispersity index (Mw/Mn)

^cDegree of polymerization

Transformation of cellulose I to cellulose II

The transformation of cellulose I (Cell I) to Cell II upon the regeneration of alkaliized pulp (rAC) is a measure of the transformation of Cell I to alkali 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, 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 $1477\text{--}1464\text{ cm}^{-1}$ and at $379\text{--}352\text{ cm}^{-1}$, Fig. 4. Agarwal (2017) has used the ratio $577\text{--}1096\text{ cm}^{-1}$. 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 (Eq. 1) was chosen for this evaluation. The change of intensity at 577 cm^{-1} , which clearly illustrates the structural change of the cellulose when applying the different alkalization settings in the present study, is shown in the "Appendix" (Fig. 7). The evaluation was complemented with the approach for amorphous cellulose C_a from the same reference (Eq. 2), and the completion to 100% was interpreted as the proportion of Cell I (Eq. 3). This value for Cell I was, on average, 8% units lower than the Raman crystallinity index $X_{\text{C}_{\text{Raman}}}$ established by Schenzel et al. (2005) ($\text{Cell I} = 1.0422 X_{\text{C}_{\text{Raman}}} - 8.032$, $R^2 = 0.9841$). The approach by Schenzel et al. (2005) uses the ratio of the intensities

at 1481 cm^{-1} and 1462 cm^{-1} as an expression for the degree of crystallinity of partially crystalline Cell I samples.

$$\text{Cell II [\% of crystalline share]} = \frac{\frac{I_{577}}{I_{1096}} - 0.009}{0.0013} \quad (1)$$

$$C_a [\% \text{ of total cellulose}] = \frac{I_{1380}}{I_{1096}} \times 100 \quad (2)$$

$$\begin{aligned} \text{Cell I [\% of total cellulose]} \\ = (100 - C_a) \times \frac{100 - \text{Cell II}}{100} \end{aligned} \quad (3)$$

The degree of transformation (D_T) of the pulp into alkali cellulose was calculated as an increase in Cell II upon alkalization and regeneration (Eq. 4).

$$D_T = \frac{100 \times (\text{Cell II}_{\text{rAC}} - \text{Cell II}_{\text{DWP}})}{100 - \text{Cell II}_{\text{DWP}}} \quad (4)$$

According to the literature, alkali concentrations of $\geq 16\text{ wt\%}$ aq. NaOH at $20\text{ }^\circ\text{C}$ 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% (Fig. 5). 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

Fig. 4 Raman spectra of the long-fiber sulphite pulp (LFs) in native form and after alkaline extraction with 18 wt% aq. NaOH at $50\text{ }^\circ\text{C}$ (LFs 18/50). Bands of interest for evaluation of cellulose structure are marked

Fig. 5 Transformation of Cell I to Cell II of different pulps (LF—long fiber, SF—short fiber, s—sulphite, k—kraft, x—high xylan) 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

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, *LFs* 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), *SFk* reached the same level as *LFs*. 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 conversion. 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 *LFs* and *SFk*, a maximum of transformation was achieved using 14 wt% aq. NaOH at 20 °C. *SFk-x* reached that transformation level at 18 wt% aq. NaOH. The earlier and more pronounced transformation of *LFs* and *SFk* can be related to the highest degree of C_a (*LFs*) and the lowest degree of Cell II (*SFk*) (cf. Table 3), which are supposed to favor the reactivity of a pulp.

Optimizing the alkalization step

The present study identified typical differences between conventional dissolving wood pulp (DWP) and, thus, room for process optimization in the process step of steeping with alkali. The long-fiber sulphite pulp (*LFs*) with an initially low content of xylan and high PDI reached the highest purity from hemicelluloses (7–8 mg/g, cf. Table 3 and Fig. 2c) 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 (Fig. 1). 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 (*SFk* and *SFk-x*, 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 Fig. 2a, b). Residual xylan in *SFk-x* 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 (*SFk-x* resp. *SFk*). 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 *LFs* and *SFk* to Cell II via Na-Cell occurred already with 14 wt% aq. NaOH at 20 and 35 °C. *SFk-x* needed 18 wt% aq. NaOH for the maximum transformation. *LFs* 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 *SFk*, and especially *SFk-x*, 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 *SFk* 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. *SFk-x* 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” (Fig. 8).

Conclusions

It was found that different 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 initial properties of the pulps determined the individual absolute level of extraction for each setting as the swelling of the carbohydrate structure passed through the maximum range of different settings. The specific level of extraction was found to depend on the initial homogeneity and purity of the pulp measured as content of xylan and PDI. The results indicate that each pulp has different steeping settings that are optimum for the properties of the alkali cellulose or its regenerate. These properties are purity, yield, and

degree of transformation. Extracting with 18 wt% aq. NaOH for all pulps investigated led to an optimal alkalization result for yield, purity, and conversion. 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 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. It would be of interest to investigate a narrower range of steeping settings that mirror today’s viscose production conditions using this pulp as proof-of-concept. Moreover, it would be of interest to investigate the extent to which extracted xylan is degraded at temperatures up to 50 °C.

It was also found that the more uncommon analysis of R18 at 50 °C gives 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.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Appendix

See Figs. 6, 7 and 8.

Fig. 6 Molecular weight distribution of pulps (LF—long fiber, SF—short fiber, s—sulphite, k—kraft, x—high xylan) and their regenerate after alkalinization 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

Fig. 7 Raman-intensities at a small selection of wavenumbers for short-fiber kraft pulp (SFk-x) and its alkalinized residues. Alkalinization was done with 10, 14, or 18 wt% aq. NaOH at 20, 30, or 50 °C, respectively

Fig. 8 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** LFs—long-fiber sulphite pulp; **c, d** SFk—short-fiber kraft pulp; **e, f** SFk-x—short-fiber kraft pulp with high xylan

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