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Carbohydrate loss reactions during viscose manufacture

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Abstract

The focus of this thesis was laid on carbohydrate degradation reactions in different steps of viscose fiber production. Particularly close attention was given here to the cellulose degradation kinetics during the alkaline steeping and during spinning under acidic conditions.

Degradation kinetics during the steeping step was examined using an industrial beech-sulfite pulp. The influence of treatment temperature and time was investigated at a constant alkali concentration of 18 % NaOH. Further, the formation of degradation products in the insoluble residues as well as in the press lye was monitored. The obtained data formed the basis for a model, containing all three reaction types, which cellulose undergoes in alkaline media. For the first time secondary peeling occurring after alkaline hydrolysis of the cellulose chains was considered.

For the investigation of the degradation reactions during cellulose regeneration in the spinning bath viscose fibers were manufactured using beech sulphite pulp. The fibers were treated at varying temperatures in a model spinning bath and the degradation kinetics was monitored. Additional to standard viscose, hemicellulose-enriched fibers obtained by using hemicellulose-containing process lye were investigated. Changes in crystallinity and composition of the degraded fibers and the formation of soluble degradation products were monitored.

The influence of the temperature, cellulose degree of polymerization, acid concentration and the hemicellulose content in the viscose on the intrinsic viscosity in the fiber and the formation of soluble organic compounds in the spinning bath during the spinning process were investigated. The design of experiments and the analysis of the results were achieved via Design Expert.

Xylans of high purity was isolated from the raw material wood, from intermediate production stages and from final bleached paper and dissolving pulps. Beech sulphite pulp and Eucalyptus kraft pulp were used for comparison.

Investigations with different methods for xylan extraction gave a more complete picture of the biopolymer. Nitren and Dimethyl sulfoxide (DMSO) were investigated giving different yields and product properties. DMSO extraction led to a water soluble product, whereas the alkaline Nitren solution provoked the cleavage of acetyl groups. Additionally, the molar mass

distribution, carbohydrate composition and structure of the obtained xylans and the extraction residuals were examined by SEC, HPLC and further advanced analytical methods.

Zusammenfassung

Der Fokus dieser Arbeit wurde auf die Abbaureaktionen von Kohlenhydraten in den unterschiedlichen Schritten der Viskosefaserproduktion gelegt. Dabei wurde insbesondere die Kinetik des Celluloseabbaus sowohl während der alkalischen Maische, als auch beim Spinnen unter sauren Bedingungen berücksichtigt.

Die Versuche zur Bestimmung der Reaktionskinetik in der Maische wurden mit einem industriellen Buchensulfit-Zellstoff durchgeführt. Bei gleichbleibender Alkalikonzentration von 18 % NaOH wurde der Einfluss von Temperatur und Behandlungszeit untersucht. Auch die Bildung der Reaktionsprodukte wurde sowohl in den unlöslichen Rückständen, als auch in der Presslauge verfolgt. Auf Grundlage der erhaltenen Daten wurde ein Modell erstellt, das die drei Reaktionstypen beinhaltet, welche Cellulose in alkalischen Medien eingeht. Erstmals wurde der Abbau durch sekundäres Peeling berücksichtigt, der nach der Spaltung der Celluloseketten durch die alkalische Hydrolyse einsetzt.

Für die Untersuchung der Abbaureaktionen während der Regeneration der Cellulose im sauren Spinnbad wurden aus dem Buchensulfit-Zellstoff Viskosefasern hergestellt. Diese wurden in einem Modellspinnbad bei unterschiedlichen Temperaturen behandelt und die Kinetik der Abbaureaktionen wurde bestimmt. Zusätzlich zu Standardfasern wurden auch mit Hemicellulose angereicherte Fasern untersucht, die unter Verwendung von Betriebslaugen hergestellt wurden. Die Änderungen von Kristallinität und Zusammensetzung der abgebauten Fasern und die Bildung der löslichen Abbauprodukte wurden untersucht.

Der Einfluss von Temperatur, Polymerisationsgrad der Cellulose, Säurekonzentration und Hemigehalt in der Viskose auf die Grenzviskosität in der Faser und Bildung von löslichen organischen Verbindungen im Spinnbad während des Spinnprozesses wurde untersucht. Die Versuchsplanung und Auswertung der Ergebnisse erfolgte mit Design Expert.

Xylane mit hoher Reinheit wurden aus dem Ausgangsprodukt Holz und den daraus hergestellten Zellstoffen isoliert. Es wurden sowohl die fertig gebleichten Papier- und Chemiezellstoffe, als auch ihre Vorstufen verwendet. Buchensulfit-Zellstoff und Eukalyptus Kraft-Zellstoff wurden verglichen. Durch die Verwendung von zwei unterschiedlichen Lösungsmitteln, Nitren und Dimethylsulfoxid (DMSO) für die Extraktionsversuche wurden unterschiedliche Ausbeuten und Produkteigenschaften von Xylan erhalten. Extraktion mit DMSO ergab ein wasserlösliches Produkt, während in der alkalischen Nitren-Lösung

Acetylgruppen abgespalten wurden. Die Charakterisierung der erhaltenen Xylane erfolgte mit Hilfe von HPLC, SEC und weiterer moderner Analysemethoden und lieferte Informationen über die Molmassenverteilung, Zusammensetzung und Substituentenverteilung.

List of publications

Paper

1. Mozdyniewicz, DJ, Sixta, H (2012) Carbohydrate degradation reactions during alkaline steeping of dissolving pulp – Influence of air exclusion. Lenzinger Berichte 90, 103 – 107

2. Mozdyniewicz, DJ, Nieminen, K, Sixta, H (2013) Alkaline steeping of dissolving pulp. Part I: Cellulose degradation kinetics. Cellulose 20 (3), 1437 – 1451

3. Mozdyniewicz, DJ, Schild, G, Sixta, H (2014) Alkaline steeping of dissolving pulp. Part II: Soluble compounds in the press lye. Cellulose 21 (4), 2889 – 2900

4. Mozdyniewicz, DJ, Nieminen, K, Kraft, G, Sixta, H (2015) Degradation of viscose fibers during acidic treatment. Cellulose DOI 10.1007/s10570-015-0796-7

Contributions of the author

Papers 1 – 4: Experiments, analysis, first version of manuscript, except the modelling

Poster presentations

1. Mozdyniewicz, DJ, Sixta, H (2011) Carbohydrate degradation reactions during alkaline steeping of dissolving pulp. 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31

2. Mozdyniewicz, DJ, Sixta, H (2011) Carbohydrate reaction kinetics during alkaline steeping of dissolving pulp. 14th Austrian Chemistry Days, Linz, Austria, September 26-29

3. Mozdyniewicz, DJ, Sixta, H (2012) Carbohydrate loss reactions during viscose manufacture. 12th European Workshop on Lignocellulosics and Pulp, Espoo, Finland, August 27-30

4. Mozdyniewicz, DJ, Nieminen, K, Schild, G, Sixta, H (2014) Carbohydrate loss reactions during viscose manufacture. 13th European Workshop on Lignocellulosics and Pulp, Sevilla, Spain, June 24-27

Oral contributions

1. Mozdyniewicz, DJ, Sixta, H (2012) Carbohydrate reaction kinetics during alkaline steeping of dissolving pulp. 8. Minisymposium Verfahrenstechnik, Linz, Austria, May 2
2. Mozdyniewicz, DJ, Schild, G, Sixta, H (2013) Changes in structure of the biopolymer xylan during pulping and bleaching. 3rd EPNOE International Polysaccharide Conference, Nice, France, October 21-24

Contents

Background

Viscose fiber production

The beginnings of the viscose fiber production process date to the early 1900s. It was initially developed for the production of lamp filaments. Several modifications of the process were needed to make a production of textile yarn possible.Although the process has been known for more than 120 yeas now, improvements are still of high economical interest, such as increasing the fibre yield or the isolation of by-products of high added value. Viscose production is expected to continue, until an alternative, more sustainable and economic process becomes available, which will provide fibers of equivalent or superior properties for any particular applications (Röder et al. 2013).

A pulp of high cellulose content is required for the process. For the most part lignin and hemicelluloses are removed before the pulp enters the fiber production. Sulphite cooking and the subsequent bleaching stages were developed and optimized over time to enable a production of dissolving pulp with high purity and optimal properties.

During the fiber manufacturing process pulp components are exposed to varying conditions. Cellulose is subjected to a broad range of different reaction types, mostly leading to an undesired yield loss. In the first step of the viscose fiber production pulp is mixed with strong alkali to dissolve the remaining hemicellulose and to convert cellulose I into cellulose II in order to enhance the reactivity (Kolpak et al. 1978; Krässig 1993). In that, and the subsequent aging stage the degree of polymerisation (DP) required for further processing is adjusted. In the following step, xanthation of the cellulose takes place, resulting in an alkali soluble polymer. After the addition of dissolving lye viscose dope is obtained, which is then filtered and ripened to obtain optimal properties for the subsequent fiber spinning.

Under strong acidic conditions cellulosic fibers are regenerated in a spinning bath. Subsequent washing, drying and cutting leads to a product processible in yarn production and further in the textile indurstry (Götze 1967).

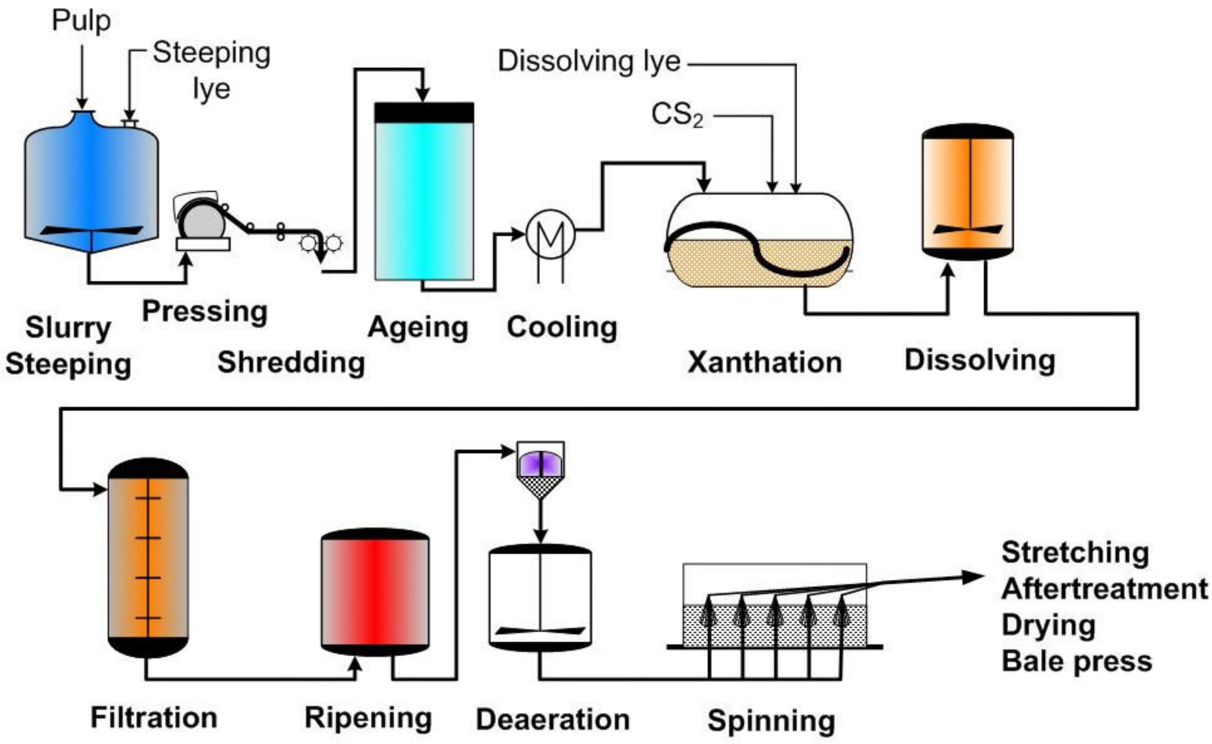

Figure 1 Basic scheme of viscose fiber production (image kindly supplied by Lenzing AG)

Cellulose reactions in alkaline media

Strong alkaline conditions are prevalent in large part of the viscose process. Relatively long lasting exposure of the carbohydrates to alkaline media results in considerable degradation causing undesired yield losses.

The idea of the successive shortening of the cellulose molecule in strong alkaline solutions came up as a part of the investigations of swelling and dissolution in cold alkali (Davidson 1934). Several years later, the accessible reducing end group was suggested as the starting position for the degradation reaction (Richtzenhain et al. 1954). Subsequently, isosaccharinic acids were identified as the main cellulose degradation products (Richards and Sephton 1957). Finally, an exact reaction mechanism was introduced for the peeling and stopping reactions (Machell and Richards 1957).

Generally, three possible reaction types contributing to cellulose degradation in alkaline media can be distinguished.

1. The peeling off reaction (beta-elimination) of the reducing end group and their conversion to isosaccharinic acids is the most important contribution to yield loss during the

steeping reaction (Figure 2). The accessible reducing end group of the cellulose is transformed to an enediol via keto-enol tautomerism, which in the case of ketoses and aldoses is known as Lobry de Bruin-Alberda van Ekenstein transformation. Under alkaline conditions, the 2,3-enediol is deprotonated to an enolate, which promotes β-alkoxycarbonyl elimination at the C-4 carbon atom, followed by benzilic acid rearrangement to form α- or β-isosaccharinic (3-deoxy-2-C-(hydroxymethyl)-pentonic acid) acid. Retroaldol reactions of the enediol may lead to additional short chain degradation products (Lai and Ontto 1996).

2. The second mechanism is the stopping reaction. The deprotonation of the 1,2-enediol causes β-hydroxycarbonyl elimination. After benzilic acid rearrangement, the formation of an alkali-stable glucometasaccharinic acid end group is observed (Machell and Richards 1957). The stopping or termination reaction was shown to occur only with alkali concentrations sufficiently high to produce the dianionic intermediate, whereas the peeling-off reaction is effective through both the mono- and the dianions (Young et al. 1972). Thus, the stopping reaction rate is more increased with rising alkali concentrations than the peeling reaction (Lai and Sarkanen 1969). The pathway of the reaction is illustrated in Figure 2. Besides chemical stopping reactions, physical stopping occurs, when the end-wise degradation reaction reaches an inaccessible, crystalline region of the cellulose fibrils. Both, the chemical and physical stopping reactions account for the total chain termination reaction.

3. Alkaline hydrolysis is another type of cellulose degradation reaction. It usually does not occur at temperatures below 140 °C in a detectable scale. In contrast to the endwise peeling, this cellulose chain cleavage leads to a rapid decrease in DP. The mechanism of the hydrolysis was found to follow an internal nucleophilic substitution. After a deprotonation of the glucoside, the ionic intermediate is converted to degradation products (Lai 1981). The random chain scission affords the formation of new reducing end groups accessible to secondary peeling, which further leads to an undesired yield loss.

The ratio of the peeling and stopping reaction constants serves as a crucial parameter for the assessment of the applied reaction conditions. The k_p/k_s ratio was influenced by temperature, concentration and the used base (Colbran 1961). Further, REG concentration, respectively the DP, of the polysaccharide effects the extent of the yield loss, as increased number of molecules results in a higher number of starting points for the peeling reaction (Johansson and Samuelson 1975).

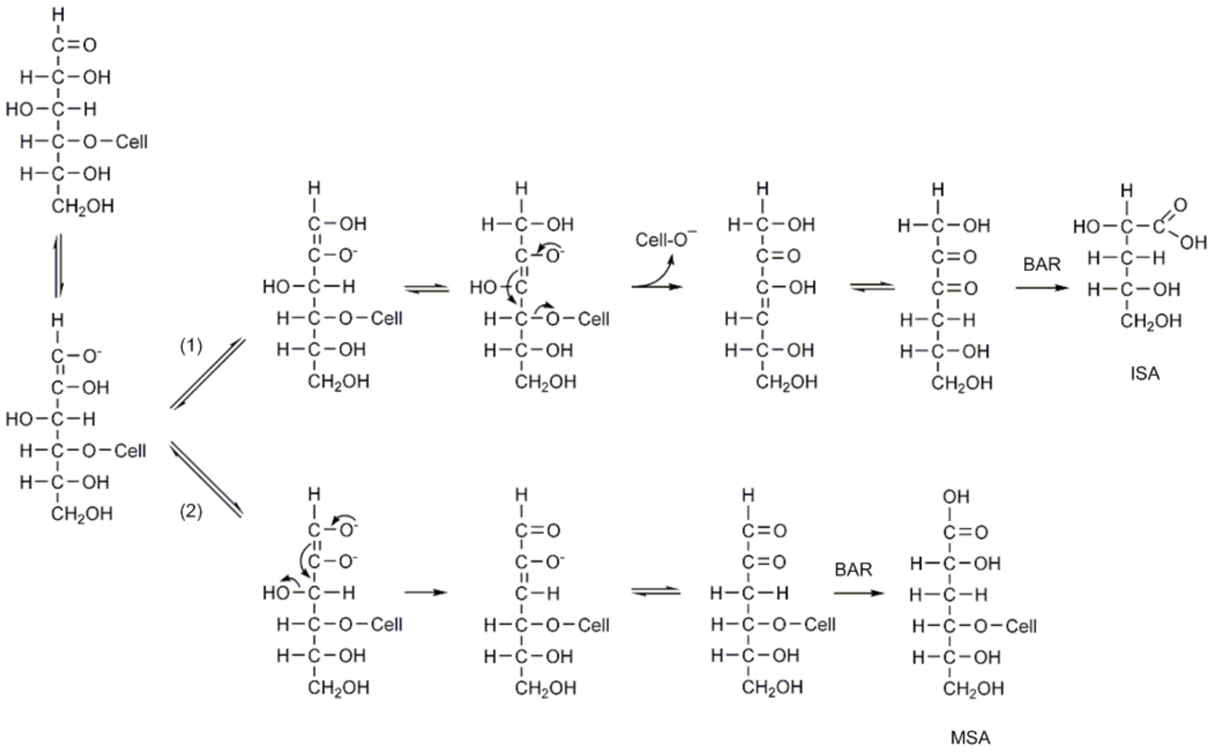

Figure 2 Cellulose reactions and the main reaction products in alkaline media: (1) peeling reaction path, (2) stopping reaction path (*BAR* benzilic acid rearrangement, *ISA* isosaccharinic acid, *MSA* metasaccharinic acid (Mozdyniewicz et al. 2014) ©Springer

The consideration of the reaction mechanisms presented above is sufficient for the steeping step, as very low amounts of oxygen are present in the steeping lye. During the subsequent aging of alkalicellulose the adjustment of the cellulose degree of polymerization (DP) is performed. Treatment time, temperature, lye concentration, press weight ratio (PWR), oxygen pressure as well as the pulp composition, the content of metal ions and the previous treatment at the bleaching stage have an influence on the reaction rate. For industrial purposes aging is performed at 40 – 50 °C with a reaction time of about five hours. Thereby a reduction of the DP from 400 – 850 to 250 – 350 occurs.

In the case of alkali cellulose aging degradation was shown to follow a radical chain mechanism with the involvement of the air oxygen (Entwistle et al. 1949). The autoxydation of the carbohydrates may occur during the steeping step when oxygen is dissolved in the lye. Thereby the oxygen is consumed by the reaction.

Cellulose reaction kinetics

During the alkaline pulping temperatures of >120 °C induce a high extent of cellulose hydrolysis. Random cleavage of the carbohydrate chains takes place due to the alkaline hydrolysis resulting in a DP reduction. However, the hydrolysis reaction rate is negligible at lower temperatures (Lai 1979). Nevertheless, secondary peeling at the newly created reducing end groups takes place contributing to undesired yield losses (Franzon and Samuelson 1957; Nevell and Zeronian 1985).

At temperatures below pulping conditions, the contribution of alkaline hydrolysis is decreasing with decreasing treatment temperature. Therefore, the first attempts of cellulose degradation modeling included the influence of peeling, stopping, and the concentration of REGs on the amount of the material lost (Haas et al. 1967; Young et al. 1972). Most of the recently published work dealing with degradation models was performed to reveal the behavior of cellulose under radioactive waste repository conditions (Van Loon and Glaus 1997, 1998; Van Loon et al. 1999; Glaus et al. 1999; Glaus and Van Loon 2008). The initial model was used in those papers, as the experiments were performed at room temperature and therefore alkaline hydrolysis was not taken into account.

An alkaline hydrolysis term was added to the original equation in later studies (Pavasars et al. 2003). However, the reaction rate under ambient conditions was found to be too low for determination of its value (Glaus and Van Loon 2004).

So far, most of the studies of degradation kinetics were limited to cellulose behavior during cooking stage and investigations of conditions applied during viscose fiber manufacture were scarce.

An improved model of cellulose degradation kinetics including secondary peeling occurring after chain cleavage due to hydrolysis was introduced by Testova et al. (Testova et al. 2014).

In the presented approach, the fraction of degraded cellulose units by the endwise peeling (P) is dependent on the initial amount of the reducing end groups (R):

$$\frac{dP}{dt} = k_p R \qquad \text{I}$$

The amount of the peeled cellulose is reduced due to the stopping reaction and increased due to alkaline hydrolysis

$$\frac{dR}{dt} = -k_s R + k_h(\Gamma_0 - P - H) \qquad \text{II}$$

the initial amount of the carbohydrates (Γ_0) is reduced by the material lost due to peeling (P) and hydrolysis (H), whose rate is proportional to the amount of non-degraded material

$$\frac{dH}{dt} = k_h(\Gamma_0 - P - H) \qquad \text{III}$$

Solving the system of three differential equations setting initial conditions $P(0) = H(0) = 0$ and $R(0) = R_0\Gamma_0$ by determination of the total degraded material $D = P + H$ resulted in the following equations

$$D = \Gamma_0\left(1 - \left(\frac{1}{2} + \gamma\right)e^{-(\alpha+\beta)t} - \left(\frac{1}{2} - \gamma\right)e^{(\alpha-\beta)t}\right) \qquad \text{IV}$$

with

$$\alpha = \frac{1}{2}\sqrt{(k_s - k_h)^2 - 4k_h k_p} \qquad \text{V}$$

$$\beta = \frac{1}{2}(k_h + k_s) \qquad \text{VI}$$

$$\gamma = \frac{k_h + 2R_0 k_p - k_s}{2\sqrt{(k_h - k_s)^2 - 4k_h k_p}} \qquad \text{VII}$$

where k_p is the first-order rate constant for the peeling reaction, k_s is the first-order rate constant for the stopping reaction and k_h represents the rate constant of alkaline hydrolysis. If the fraction of degraded cellulose units is expressed by $P = \frac{D}{\Gamma_0}$, the equation simplifies to

$$P = \left(\frac{1}{2} + \gamma\right)e^{-(\alpha+\beta)t} - \left(\frac{1}{2} - \gamma\right)e^{(\alpha-\beta)t} \qquad \text{VIII}$$

The solution of the system is determined after a transformation into one higher order differential equation and calculation of the integration constants. A detailed description is presented in the paper (Mozdyniewicz et al. 2013).

Structure and crystallinity

Generally, amorphous and crystalline fractions can be found in cellulose fibrils. Recent investigation by infrared (IR) spectroscopic methods revealed the distribution of the particular regions within and outside the cellulose fibrils (Figure 3).

The crystallites in native cellulose originally show cellulose I morphology. The conditions applied to cellulose during alkaline steeping, or strong alkali in general, cause a transformation to the cellulose II structure. The new conformation is characterized by an enhanced reactivity toward derivatization (Kolpak et al. 1978; Krässig 1993).

Looking at the molecular dimension, the essential diffenence between the conformations is given by the number of intramolecular hydrogen bonds in the monomeric unit. In the cellulose I structure, two intramolecular hydrogen bonds were found by molecular mechanics calculations, however, in the cellulose II structure, only one bond was present (Kroon-Batenburg et al. 1986; Kroon-Batenburg et al. 1990).

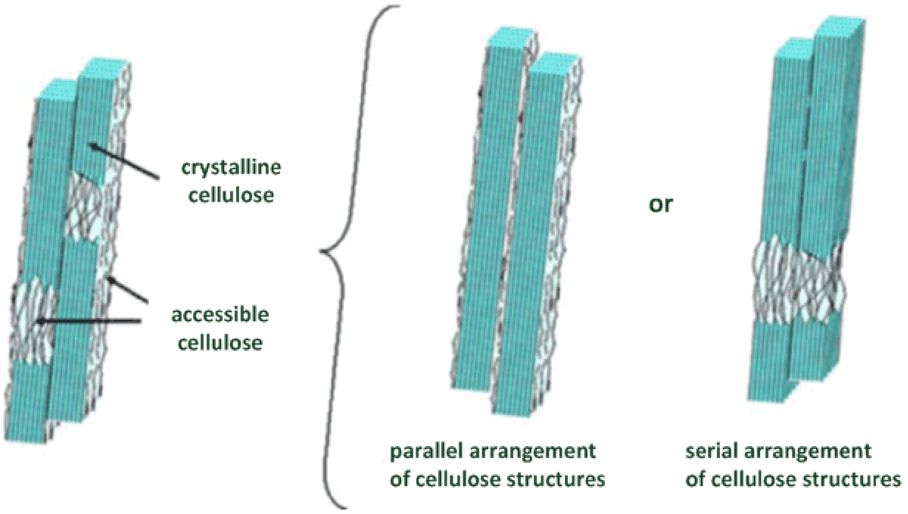

Figure 3 Structure of cellulose fibrils by IR deformation experiments (Salmén and Bergström 2009) ©Springer

Although several crystallographic investigations of cellulose II were carried out, there are still aspects that have not been unequivocally clarified:

“All X-raystudies on cellulose II indicate anantiparallel structure. Since, during the mercerization process, cellulose I also converts to cellulose II rather easily, just by swelling and therefore apparently without loss of molecular orientation, it seems a mystery how this comes about. ” (Kroon-Batenburg and Kroon 1997).

However, a distribution of the amorphous and crystalline regions in regenerated cellulose described above was confirmed in recent studies by deformation experiments and X-ray analysis (Eichhorn et al. 2005; Eichhorn and Davies 2006).

Crystallinity measurements by NMR give information of the short range order of the cellulose crystallites. The consideration of the C-4 region of the anhydroglucose enables the distinction in signal contributions of the inner-crystalline, surface crystalline and disordered material (Figure 4). The resonance positions of the crystalline regions of the cellulose II structure were initially published by Newman and provided a useful basis for further investigations (Newman and Davidson 2004). After subsequent modifications the determination of crystallinity and fibril width was implemented giving results in agreement with WAXS measurements (Ibbett et al. 2007; Ibbett et al. 2010)

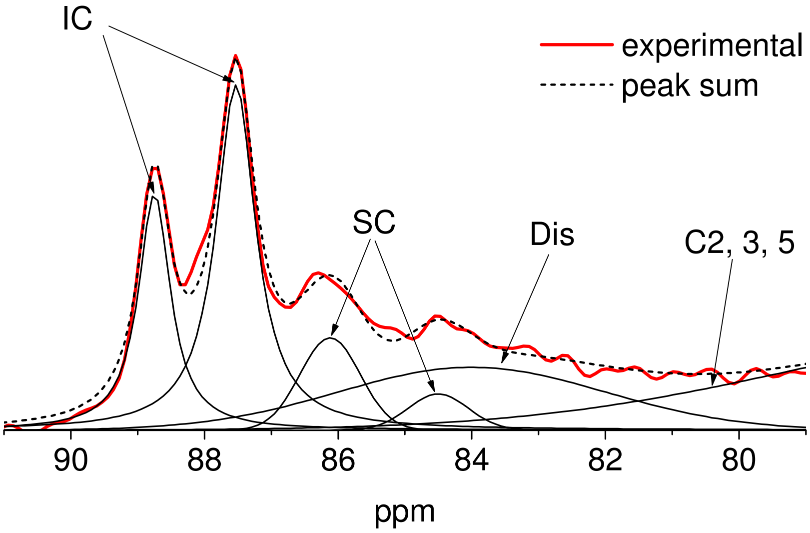

Figure 4 NMR spectrum of the C-4 region of the anhydroglucose unit (AGU) after line-shape deconvolution analysis; *IC…inner crystalline cellulose, SC…surface crystalline cellulose, Dis…disordered cellulose*

Hemicellulose reactions in alkaline media

The residual amount of hemicellulose present in the pulp used for viscose fiber production is very low due to the efficient removal in the previous process steps. Xylan makes up the largest part of the hemicellulose present in the pulp produced from hardwood for example, beech wood. Modifications of the structure and substituent distribution occur during the cooking stage and the subsequent bleaching. DP reduction and the removal of 4-O-methylglucuronic acid and acetyl groups were found to be the most significant modifications of the structure (Goeran et al. 1961; Lindström and Samuelson 1975). After dissolution during the steeping step, hemicellulose enters the lye circuit. Continuous removal of hemicellulose dissolved in the process lyes is inevitable to prevent excessive enrichment of the hemi, causing enhanced CS_2 consumption during the xanthation step.

Early efforts to characterize alkali soluble hemicellulose from beech sulfite pulp have been described previously (Bandel 1953). The samples originated from different sources within the viscose production process, and displayed slight differences in composition depending on the previous treatment. Characterization of the hemicellulose present in beech sulfite pulp and in process steeping lye was accomplished by Mais and Sixta (Mais and Sixta 2004). Enhanced formation of degradation products accurred as a result of extended residence times.

Generally, the mechanism of hemicellulose degradation in alkaline media is comparable to cellulose degradation. Formation of xyloisosaccharinic acid due to peeling proceeds until xylometasaccharinic acid is formed as a result of the stopping reaction (Aspinall et al. 1961). The amorphous form of xylan prevents degradation termination due to physical stopping. However, 4-O-methylglucuronic acid substituents along the xylan chain prohibit the progression of the peeling (Johansson and Samuelson 1977). The pathway of the xylose chain degradation was verified by alkaline treatment of xylan model compounds (Sartori et al. 2004).

Carbohydrate degradation products

Generally, glucoisosaccharinic acid was identified as the main cellulose degradation product of the peeling reaction, independent of the severety of the applied treatment (Richards and Sephton 1957; Niemelä and Sjöström 1986b). Glucoisosaccharinic acid was found to be stable for time periods of up to 3 years under alkaline conditions at an ambient temperature (Van Loon and Glaus 1998). Acetic, lactic, threonic and formic acid constituted about 10 % of the dissolved organic carbon in residual alkaline liquors after the treatment of cellulose. Harsher treatment conditions led to the formation of an increased number of acids with alkyl side groups (Johansson and Samuelson 1974; Niemelä 1987).

Several hydroxy acids were identified after alkaline cellulose treatment, mostly in low concentrations. An exhaustive overview of the degradation products of cellulose and its model substances has been recently published (Knill and Kennedy 2003).

The degradation of xylan in alkaline media results in similar residuals, as it follows an analogous reaction mechanism (Aspinall et al. 1961). Xyloisosaccharinic acid is formed predominantly. At elevated temperature, such as that used during the cooking stage, lactic and 2-hydroxybutanoic acid are the most abundant products (Niemelä 1990a). The alkaline degradation of mannan results in glucoisosaccharinic acids as the main degradation products (Niemelä and Sjöström 1986a).

Cellulose reactions in acidic media

The hydrolysis of cellulose by organic and inorganic acids has recently been of a great interest with respect to biofuel production (Aguilar et al. 2002; Gámez et al. 2006; Chandel et al. 2007; Datar et al. 2007; Sun et al. 2007; Pattra et al. 2008; Kupiainen et al. 2010, 2012a, b). During the manufacture of viscose, markedly milder conditions are applied. The cellulose is regenerated from the solution in an acidic medium at an ambient temperature during fiber spinning (Götze 1967).

Although cellulose hydrolysis proceeds by the random cleavage of glycosidic bonds, a definite determination of the reaction kinetics proved difficult, due to its structural characteristics (Joksimovic and Markiovic 2007). Crystalline and amorphous regions contribute to different extents to the degradation pattern. An initial rapid cleavage of the amorphous parts is followed by a considerably slower degradation of the crystallites (Sharples 1954, 1957). The reaction proceeds until the Level-off-DP is reached (Calvini 2005). The residual crystallites are furhter degraded at the edges (Sharples 1957). This concept was confirmed for cellulose II structures in subsequent work (Lin et al. 1991). Later, the idea of recrystallization in cellulosic fibers after acid hydrolysis was introduced (Ibbett et al. 2008).

The idea of fast hydrolyzing weak links was initially introduced by Meller (Meller 1960b, a). During cellulose processing as well as due to natural aging, ketones, aldehydes and acids are formed (Schleicher and Lang 1994; Potthast et al. 2006). The oxidized anhydroglucose units are more fragile compared to 1,4-β glucosidic links and are cleaved with a higher degradation rate (Klemm et al. 1998).

Attempts to describe the kinetics of heterogeneous cellulose hydrolysis were further undertaken by Marx-Figini (Marx-Figini 1983, 1987). A more precise model was introduced in a later work, describing the aging of paper (Emsley et al. 1997). Due to an unsatisfactory physical explanation of the occuring phenomena model modification was inevitable, resulting in the inclusion of the Level-off-DP value (Calvini et al. 2008; Calvini 2012, 2014). In his latest paper, Calvini encouraged to the further development of the existing cellulose hydrolysis equations, with regards to using variables with an obvious physical meaning (Calvini 2014). Accordingly, there is still potential for improvement of the models describing the course of cellulose hydrolysis.

Hemicellulose reactions in acidic media

The first attempts to describe hemicellulose hydrolysis kinetics were undertaken by Saemen (Saemen 1945). A mechanism similar to that of cellulose degradation was proposed for hemicellulose hydrolysis. Again, random bond cleavage was assumed to occur, however, with a higher reaction rate due to the amorphous character of the substrate. In some cases, varying reaction rates were found to be dependent upon the degradation progress (Kobayashi and Sakai 1956). The works on this topic were summarized by Jacobsen (Jacobsen and Wyman 2000). Generally, the hydrolysis of hemicellulose has been given much less attention compared to cellulose.

Xylan isolation

The implementation of the biorefinery concept even in existing, well-established production sites is gaining in importance due to economic and environmental reasons. In the pulp industry, the exploitation of products previously considered to be waste and then discarded has become inevitable to ensure the competitiveness of the production sites. Besides lignin, hemicellulose has been recently of growing interest as a source of potential, valuable products.

Xylan is the main hemicellulose present in hardwood. During dissolving pulp production it is extracted before or after the cooking stage. As a consequence of the harsh processing conditions, monomer sugars are present in the cooking liquor due to carbohydrate degradation. The sugars may be converted to ethanol for fuel production or for use in the food industry, as it is done for xylitol, to name but one example (Eroma et al. 2006). Furfural is another interesting xylan derived product with numerous potential applications (Li et al. 2013; Cai et al. 2014).

In contrast to dissolving pulp production, minimum xylan degradation is desired during paper pulp manufacturing. A high molar mass and hemicellulose yield enhance the quality of the produced paper.

The properties and behavior of the hemicelluloses have been of great interest over the past decades, it was therefore isolated by the use of different kinds of solvents and extensively characterized by various analytical methods. Several wood species as well as various pulps have been used as substrates thus far (Timell 1960; Goeran et al. 1961; Kürschner and Karácsonyi 1961; Ebringerová and Hromádková 1986; Evtuguin et al. 2003; Mais and Sixta 2004). Differences in average molar masses and carbohydrate composition and the presence and distribution of side groups were found.

Alkaline extraction is the most common method of xylan isolation in a lab scale as well as an industrial scale. High yields coincident with high purity characterize the hemicellulose isolated under alkaline conditions (Thompson et al. 1963; Ross and Thompson 1965). However, the high pH of the solvent may lead to the cleavage of acetyl groups and the loss of the native state of the hemicellulose (Iversen and Lindgren 1983; Laine et al. 2013).

Therefore, dimethyl sulfoxide (DMSO) was introduced as a hemicellulose solvent, leaving the substituent distribution largely unchanged (Hagglund et al. 1956). From then on, the way was paved for the successful extraction and extensive characterization of the native xylans without a loss of information due to structure changes. Previously unresolved questions were answered, especially concerning the structure and substituents of xylan from *Eucalyptus globulus*, birch wood, and beech wood (Teleman et al. 2002; Evtuguin et al. 2003).

Nitren was first introduced as a promising selective xylan solvent for upgrading paper-grade pulps to dissolving pulps. The solvent is obtained by complexation of nickel(II) hydroxide and tris-(2-aminoethyl) amine in an aqueous medium (Kettenbach and Stein 2002). Its large-scale application, although technically feasible, was proven particularly problematic due to its toxicity and a large number of washing steps required. Nevertheless, using Nitren for xylan removal has benefits, as lower chemical charge, high selectivity (at concentration < 7 %) and preservation of the cellulose I structure. Further, the properties of the isolated xylan are comparable with those of the hemicellulose obtained by alkali extraction with 14 % KOH or 10 % NaOH (Janzon et al. 2008b). A significant dependence of the extraction efficiency and yield on temperature and Nitren concentration was observed (Janzon et al. 2006; Janzon et al. 2008a; Janzon et al. 2008b; Santos et al. 2013).

Over the past few years the interest in the application of ionic liquids for biomass fractionation has grown, in particular the conversion of paper grade pulp into high purity dissolving pulp. In the recently developed Ioncell-P process hemicellulose is removed by extraction using 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) giving excellent pulp properties. Slight modifications and the use of 1-ethyl-3-methylimidazolium dimethylphosphate ([emim][DMP]) enable the production of acetate grade pulp with high purity and hemicellulose content lower that 2 %. A negligible cellulose yield loss, easily achievable recovery of pure hemicellulose, the possibility of solvent recycling make the IL-based extraction an excellent process for future application (Froschauer et al. 2013; Sixta et al. 2013; Roselli et al. 2014).

Research Questions

The purpose of this study was to investigate the carbohydrate degradation reactions leading to yield losses during viscose fiber manufacture. Avoiding undesired cellulose losses may enhance the process efficiency and its environmental impact.

The modelling of the process steps creates the basis for simulation, and as a result an improved process control is possible. For a good model, a broad range of data is required, to ensure an optimal reproduction of the process conditions.

The focus of the investigation was laid on the behavior of pulp originating carbohydrates during alkaline steeping. For cellulose to be the main component, the adaptation of a comprehensive degradation model for the process conditions based on an extensive data set was one of the targets. The identification and quantification of alkali-soluble components present in the steeping lye was another objective, as their presence in the lye circuit is inevitable and leads to undesired reactions (papers 1, 2 and 3).

During fiber spinning, cellulose is regenerated from the viscose dope under acidic conditions. The production of hemicellulose enriched fibers poses challenges to the manufacturing process, due to modified fiber properties and increased TOC formation in the spinning bath. Therefore, gaining an understanding of the degradation of hemicellulose containing fibers in acidic media was a crucial target of this work (Paper 4). In particular, the influence of the initial intrinsic viscosity, temperature and hemicellulose content on the degradation kinetics was of interest.

The influence of several variable spinning parameters on cellulose behavior and properties during and after regeneration was investigated using an experimental design. The aim was to determine the optimal spinning conditions resulting in low yield loss and cellulose degradation. The influence of several spinning parameters like temperature, acid concentration, degree of polymerization and the hemicellulose content in the spinning dope had to be investigated with regard to TOC formation and final intrinsic viscosity.

The addition of xylan to viscose fibers as well as the generation of novel bio-refinery products requires applicable hemicellulose with an easily available source. Therefore, one of the aims of this study involved the isolation of xylan from several pulp production stages, wood species and manufacturing processes (dissolving grade sulphite and paper grade Kraft pulp) and the subsequent characterization of the substrate to identify the changes occurring in structure and behavior. Nitren and DMSO were used as xylan solvents, due to the different characteristics of the resulting isolation products.

The newly found information would enable the choice of the optimal position within the production process to extract the xylan with the desired properties for possible future applications. The extractions using two differing solvents having an influence on the characteristics of the obtained fractions would lead to a wide spectrum of potential products.

Experimental

Materials

Alkaline steeping and fiber production

TCF bleached beech sulphite pulp was used for the steeping experiments and as a base material for lab scale and pilot plant viscose production. A mill sample was taken after final drying. The characteristics of the pulp are shown in Table 1.

Table 1 Properties of the initial TCF bleached sulfite pulp (Mozdyniewicz et al. 2013) ©Springer

R18 (% odp)	93.3
R10 (% odp)	87.04
η (mL/g)	530
COOH$_{\mathrm{MB}}$ (μmol/g)	24.6
COOH$_{\mathrm{FDAM}}$ (μmol/g)	13.5
Carbonyl groups$_{\mathrm{CCOA}}$ (μmol/g)	26.6
Mn (kg/mol)	31.3
Mw (kg/mol)	212.9
DP < 100 (% odp)	11.4
DP > 2,000 (% odp)	26.5
PDI (–)	10
Glucan (% odp)	91.4
Xylan (% odp)	3.1
Mannan (% odp)	0.6
CrI$_{\mathrm{NMR}}$ (% odp)	52
CrI$_{\mathrm{Raman}}$ (% odp)	54
Cellulose I$_{\mathrm{Raman}}$ (%)	97

All the chemicals used for the experiments and analyses were purchased from common suppliers.

Xylan isolation

Eucalyptus (*Eucalyptus globulus*) and beech (*Fagus sylvatica*) wood were used for the isolation of xylan. The chips were air dried and coarsely ground. Further, several pulps were used for the investigation. A beech sulphite pulp was used with one sample taken directly after the cooking and one TCF bleached sample. The Kraft eucalyptus paper grade pulp was used after the first delignification step and after ECF.

Methods

Alkaline steeping

A sodium hydroxide solution of 18 ± 0.02 wt% was used for the steeping experiments. The pulp was placed in a round-bottom flask equipped with a magnetic stirrer and a thermometer. A pulp-to-liquor ratio of 1:60 was used. The sodium hydroxide solution was flushed with argon and adjusted to the required temperature levels of 40, 50, or 60 °C. The exclusion of oxygen was achieved by repeated evacuation and argon flushing of the apparatus before starting the experiment. For comparison purposes, a series of experiments at 50 °C was performed without air removal. After the addition of the steeping lye, the mixture was stirred vigorously for 10 min to ensure a complete mixing. A uniform impregnation of the fibers with sodium hydroxide was achieved. The xylan present in the pulp was dissolved to a great extent during this initial step. Therefore, the starting point for the modeling of cellulose degradation kinetics was chosen after the initial steeping. The pulp suspension remained in the reactor for up to 80 h. All experiments were performed at least twice for each treatment time. Subsequently, the suspension was filtered on a glass filter funnel (porosity 4), and the solid residue was neutralized with 20 % acetic acid, washed until neutral pH and quantitatively transferred into a crystallizing dish, where it was air dried. The yield of the insoluble cellulose fraction was determined after the dry content analysis. To obtain the yield loss fraction, the amount of the insoluble material after the definite treatment time was related to the cellulose yield after the initial steeping time.

The resulting filtrate contained acid-insoluble hemicelluloses as well as soluble cellulose and hemicellulose degradation products. The precipitated fraction under controlled conditions (DIN 54355) consisted mainly of xylan and will be subsequently referred to as the β-fraction. For a quantitative analysis of the β-fraction in the remaining solution, a defined amount of lye was added to an equal volume of diluted sulphuric acid (H_2SO_4:H_2O, 1:3). The solution was allowed to cool down in a water bath for 30 min. The precipitated fraction was removed by filtration. The COD (DIN 409) and TOC (EN 1484) contents were measured in the original lye as well as in the filtrate. For the isolation of larger amounts of the β-fraction, the lye was slowly poured into an equal volume of ice cooled, stirred, diluted sulphuric acid and the mixture was allowed to stand overnight. The precipitate was centrifuged and washed until it was sulphate free, and then freeze dried.

After the procedure, various soluble cellulose and hemicellulose degradation products remained in the solution. For the characterization of the hydroxy-acids, the filtrate after the quantitative determination of the β-fraction was used. The analyses were performed at the Laboratory of Applied Chemistry at the Department of Chemistry at the University of Jyväskylä. The hydroxy monocarboxylic and dicarboxylic acids were identified using a GC–MS method and quantified by a GC–FID method after a preceding trimethylsilylation (Alén et al. 1984). The method was developed for the identification of alkaline degradation products in black liquors, but the high inorganic salt content made an accurate analysis difficult. In some samples, sulphate had to be removed by precipitation with $Ba(OH)_2$.

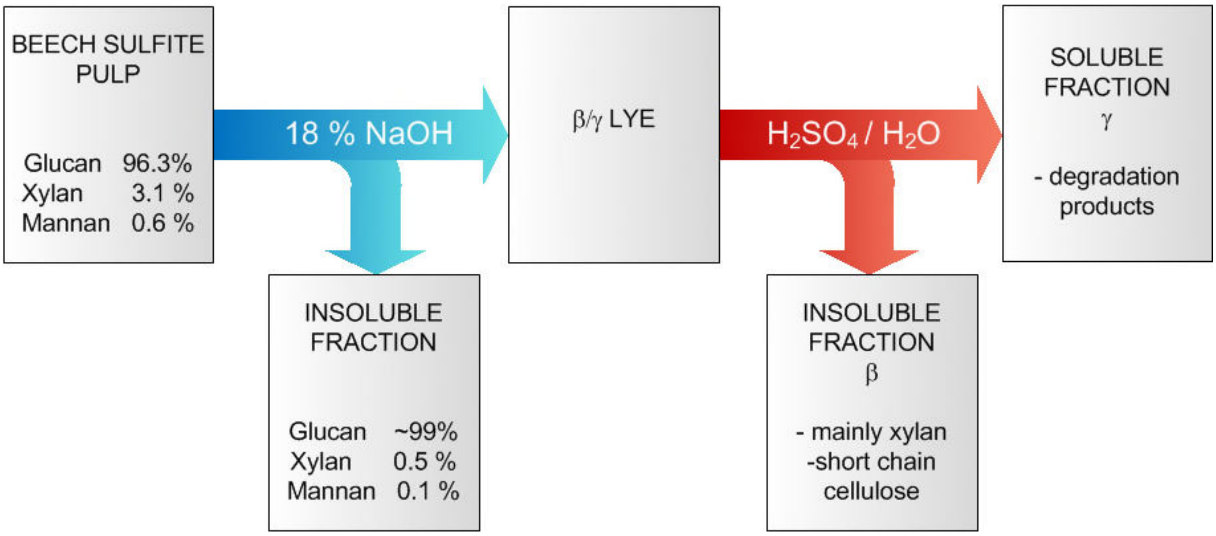

Figure 5 Fraction separation scheme (Ebringerova and Heinze 2000) ©Springer

Viscose fiber preparation

The fibers used for degradation experiments were prepared by a standard viscose dope production procedure in a pilot plant scale. The target η-values were obtained by a controlled aging of the alkali cellulose. The dope viscosity had to be adjusted for the varying cellulose DP using different cellulose concentrations resulting in altering settings during the spinning process. After spinning, the fibers were collected, washed neutral and stored cooled.

In addition to common fiber composition, xylan-enriched fibers were prepared using a hemicellulose-rich process lye as a dissolving lye (Schild et al. 2012).

For the evaluation of spinning conditions, experiments in a smaller scale were performed. Design Expert® 9 by Stat-Ease was used for the experimental design, allowing for a reduced number of trials. The viscose dope was prepared in a laboratory scale according to a modified method by Treiber (Treiber and Abrahamson 1969). The viscose solution was extruded through a 20-hole spinneret into a spinning bath on a bench-scale unit. The obtained fibers were collected and left for one hour in a defined amount of deionized water to remove the residual soluble components. Subsequently, the fibers were air-dried and analyzed. The formation of organic compounds in spinning bath and during washing was monitored by TOC measurements.

Acidic fiber degradation

The never dried fibers were, treated with a standard spinning bath at 40, 50, and 60 °C for time periods up to 292 hours in Erlenmayer flasks to determine the degradation kinetics. Therefore, a defined amount was added to the preheated spinning bath. After a certain time period, the fibers were separated from the solution and washed neutral. The yield, carbohydrate composition, and intrinsic viscosity were determined after air-drying. The TOC of the remaining solutions was measured.

Four fiber types were used for the degradation experiments. Fiber A was characterized by low DP, compared with fiber B with high initial DP. No hemicellulose was added to fibers A and B. In comparison, two hemicellulose-enriched fibers were prepared. Fiber C represented the low molecular type and contained 4.9 % hemicellulose, fiber D had a higher DP and contained 15.4 % xylan and mannan. The properties of the initial fibers are shown in Table 2 and Figure 6.

Table 2 Initial properties of the fibers used for the degradation experiments

Fiber	Hemicellulose (Xylan) [%]	η [ml/g]	DP [-]	Mn [kg/mol]	Mw [kg/mol]	PDI [-]	CrI_{NMR} [% odp]
A	0.7 (0.6)	209	498	29.3	61.7	2.1	40.9
B	0.7 (0.6)	352	838	42.5	153.1	3.6	43.2
C	4.9 (4.4)	237	564	25.7	75.7	2.9	39.4
D	15.3 (14.1)	270	643	22.4	114.5	5.1	37.5

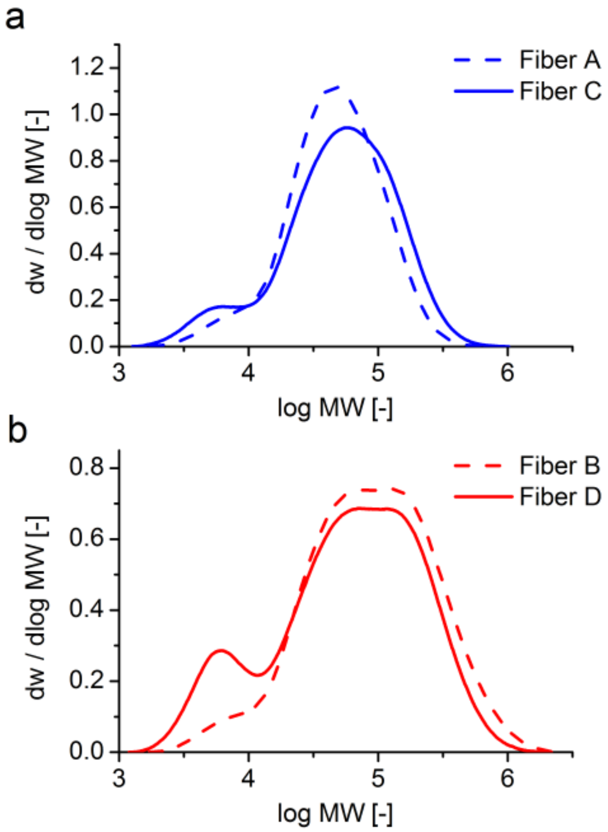

Figure 6 Initial molar mass distribution of the fibers used in the acidic degradation experiments

Xylan isolation

All the wood and pulp samples were grinded (40 mesh). Wood samples (ca. 100 g) were extracted with 1.5 L EtOH/Toluene (1:2) for 6 hours and delignified using peracetic acid (10 %) at pH 3.5, adjusted with dilute NaOH. The wood was treated for 30 – 35 min at 85 °C with a solid/liquid ratio of 1:50. After the reaction time, the mixture was cooled in an ice bath. Delignified wood was filtered, washed with deionized water and acetone/EtOH (1:1) and air dried. Pulp samples were used without any additional treatment. In Table 3 the carbohydrate composition of the substrates used is shown.

Xylan was extracted with DMSO by a method published elsewhere, slightly modified (Pinto et al. 2005). Substrates were stirred for 10 hours at 50 °C and then further for 12 hours at room temperature. The solution obtained was poured into an acidified EtOH/MeOH/H_2O mixture and stored cooled overnight. The precipitate was separated by centrifugation and freeze-dried after washing with EtOH/MeOH (Evtuguin et al. 2003).

Table 3 Carbohydrate composition of the substrate used for xylan isolation

	Glc [% ATS]	Xyl [% ATS]	Man [% ATS]	Ara [% ATS]	Rha [% ATS]	Gal [% ATS]	Σ [% ATS]
BW (extr)	37.8	17.3	1.4	0.6	0.4	0.9	58.4
BW (del)	58.6	21.6	1.9	0.6	0.4	0.9	83.9
BBS	88.2	5.3	0.9	-	0.1	-	94.4
BSP	93.4	3.1	0.7	-	-	-	97.2
EW (extr)	39.4	14.8	0.7	0.4	0.2	1.1	56.6
EW (del)	58.3	16.6	0.9	0.3	0.2	1.0	77.2
EBO	74.8	22.4	0.1	0.1	0.1	0.3	97.8
EKP	75.0	23.5	0.0	-	-	0.2	98.6

BW…beech wood, BBS…beech brown stock, BSP…beech sulphite pulp, EW…eucalyptus wood, EBO…eucalyptus brown stock after O-stage, EKP…eucalyptus Kraft pulp, (extr)…after extraction, (del)…delignified

For Nitren extraction, the stock solution was prepared as described in previous papers and diluted with deionized water to obtain the concentration required; 2.5 and 5 % solutions (1:10, w/w) were used (Janzon et al. 2006). After the addition of the Nitren solution, the samples were stored for one hour at room temperature with occasional shaking. After the expired reaction time, the remaining solid fraction was filtered off; washed with diluted NaOH, lactic acid and deionized water; and subsequently air dried and quantified. Xylan was precipitated from the Nitren solution by adjusting the pH to 3.5 with acetic acid.

The suspension was stored cooled overnight, the supernatant was removed and the precipitate was washed using centrifugation. The solid residue obtained was freeze-dried and analyzed.

Attempts were made to eliminate the residual cellulose content present in a number of samples. A fractionation by changes of the pH was performed (personal communication with Dos Santos, N.). The solution containing xylan was first adjusted to pH 7 by addition of formic acid. An initial precipitation of a cellulose-enriched fraction was expected due to the procedure. Xylan was assumed to remain dissolved until pH of 3 was reached. The residual precipitates were washed by centrifugation and subsequently freeze-dried.

For the SEC measurements, xylan extraction by 2.5 % Nitren was performed in a small scale. 0.33 g of wood/pulp was placed in a glass test tube and 5 ml of the Nitren solution were added. The suspension remained in the tube for one hour and was occasionally shaken. Subsequently, the samples were centrifuged, and filtered (PTFE, 0.45 µm) into vials. The solution was injected into the standard SEC system with 0.1 M NaOH as effluent (Mais and Sixta 2004).

Analytical methods

The determination of neutral sugar monomers was performed by anion exchange chromatography (AEC) with pulsed amperometric detection (PAD) after two step total hydrolysis with H_2SO_4 according to Sixta et al (Sixta et al. 2001). Additionally, methanolysis-GC was applied for selected samples in order to evaluate the carbohydrate composition and the amount of the 4-O-methylglucuronic acid. The samples were analyzed in triplicate (Sundberg et al. 1996).The amount of carboxylic groups was determined by the methylene blue adsorption method (Philipp et al. 1965; Whistler 1963). Intrinsic viscosity measurements were performed after dissolution in cupriethylenediamine according to the SCAN-CM 15:99 method. The molecular weight distribution of the cellulosic samples was determined by size exclusion chromatography (SEC) with multiangle laser light scattering (MALLS) detection in DMAc-LiCl solution according to Schelosky et al. (Schelosky et al. 1999). The uronic acid content of the initial pulp was determined by the FDAM-method (Bohrn et al. 2006). The carbonyl group content was obtained after being labeled with fluorescent marker and compared with the SEC values (Röhrling et al. 2002). The molar masses of the acid insoluble xylans were obtained by SEC measurements after dissolution in 0.5 M sodium hydroxide (Mais and Sixta 2004).

For selected pulp samples, Level-off-DP values were determined after boiling in an EtOH:H_2O mixture (Sarkov 1961).

The Level-off-DP of the fibers was determined by the method described by Klemm (Klemm et al. 1998).

Crystallinity measurements

Most of the samples were analyzed by NMR. Therefore, the samples were fitted into 4 mm oven-dry zirconium oxide MAS rotors for subsequent ^{13}C CP-MAS NMR analysis. The spectra were acquired on a Bruker AvanceDPX300 NMR spectrometer, operating at a 75.46 MHz ^{13}C NMR resonance frequency. The spectrometer was equipped with a 4 mm ^{1}H/BB CP-MAS probe, the sample spinning speed was 4 kHz, and ^{1}H decoupling was afforded by the SPINAL-64 pulse sequence. The cellulose ^{13}C CP-MAS NMR spectra were analyzed by line-shape deconvolution of the C4 signal region. All line-shape analyses were performed with the Solver tool in MicrosoftExcel^{TM}. The line-fitting of the AGU-C4 resonance was performed according to Ibbett (Ibbett et al. 2007; Ibbett et al. 2010). The resonance positions described by Newman were used for calculation (Newman and Davidson 2004).

The degree of crystallinity (CrI) and the crystal size of selected pulp samples at Level-off-DP were determined by WAXS measurements. The air-dried powder was dissected between PET-foils and sealed air-tight with silicon. The WAXS measurements were conducted with a D5000 two-circle diffractometer (Bruker-AXS) in symmetrical transmission geometry with a focusing Ge(111) primary monochromator with Cu-K_α-beam ($\lambda = 0.15406$ nm) at 30 mA and 40 kV. The diffractogram was recorded in a 2θ-angle range of 4°-104° (interval $\Delta 2\theta = 0.2°$, recording time / $\Delta 2\theta$: 55 s). The sample was rotated perpendicularly at 15 rpm and each sample was measured three times. The spectrograms were analyzed with the IAP-software WAXS7.

Microscopy

For the SEM analysis the pulp samples were disintegrated in deionized water and freeze-dried. Single fibers were fixed on a sample holder with adhesive tape and subsequently sputtered with Au/Pd (Okamoto and Meshitsuka 2010). The prepared samples were examined by high-resolution scanning electron microscopy at a 500x and 10,000x magnification with a Hitachi S4000 SEM (FE-SEM) applying an acceleration voltage of 8 kV.

Ultrastructural observations of the fibers were performed with a Tescan Vega SEM with a tungsten cathode system using an acceleration voltage of 10 – 20 kV.

Selected untreated and degraded fiber samples were investigated using the optical microscope Olympus BX5 with an XC50 camera using transmitted light mode.

Results

Alkaline steeping of dissolving pulp

Cellulose degradation kinetics

Paper 2

The degradation kinetics under steeping conditions was described using a model including the cellulose degradation due to secondary peeling occurring after chain cleavage due to hydrolysis, also referred to as Model III (Mozdyniewicz et al. 2013).

A comparison of the developed model (Model III) with previous models I and II described in the literature was performed (Haas et al. 1967; Young et al. 1972; Van Loon and Glaus 1997; Pavasars et al. 2003). In the earlier studies, Model I was used for estimation of cellulose yield loss (Haas et al. 1967; Young and Liss 1978; Van Loon et al. 1999). According to the equation used, the amount of degraded cellulose was dependent on the initial amount of reducing end groups and the rate constants of the peeling and stopping reactions. A term describing the contribution of alkaline hydrolysis was added subsequently, resulting in the enhanced predictability of Model II (Van Loon and Glaus 1997; Pavasars et al. 2003). In a later publication the negligible role of the alkaline hydrolysis at ambient temperatures was annotated by Glaus and van Loon (Glaus and Van Loon 2004).

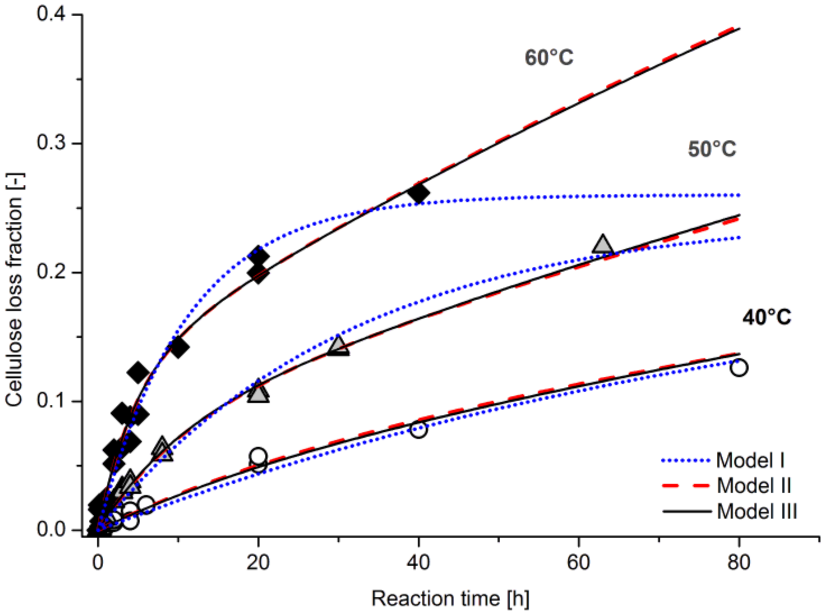

Figure 7 Comparison of different cellulose degradation models (Mozdyniewicz et al. 2013) ©Springer

Generally, R² ~ 0.99 was found for fitting the experimental data with all the equations used. The difference between the models can be found in varying explanation of the particular reactions and their contribution to cellulose loss. In Figure 7 the curves obtained after fitting the experimental data with all models described above are shown. Model II was in good agreement with the experimental data. However, alkaline hydrolysis was found to be negligible at temperatures below 90 °C, therefore an overestimation of the hydrolysis contribution could not be avoided in this case. A modification of the model, considering the yield loss due to secondary peeling was inevitable. In the new Model III, the subsequent cellulose degradation is considered and the influence of cellulose hydrolysis is minimized. Further calculations allow the determination of the contribution of the particular reaction type (Nieminen et al. 2014). The results from our data can be seen in Figure 8. The relevance of secondary peeling increases with treatment time, whereas primary peeling stops after the formation of metasaccharinic acid at the reducing end.

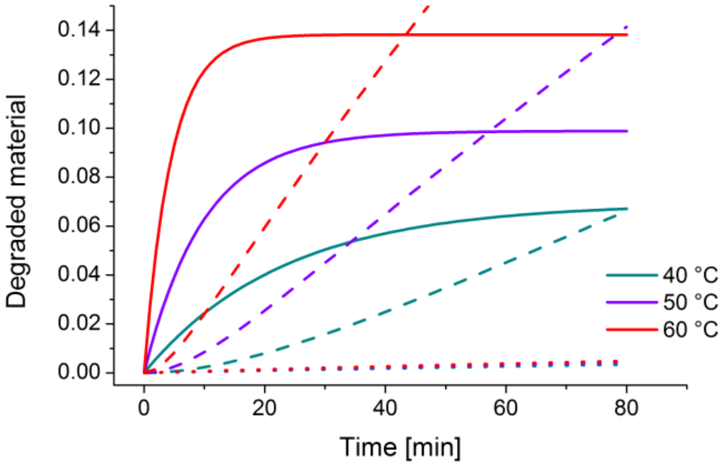

Figure 8 Partition of degraded cellulose according to the reaction type*; solid lines… primary peeling, dashed lines…secondary peeling, dotted lines…alkaline hydrolysis*

The broad range of experimental data allowed the calculation of the reaction constants, activation energies, and frequency factors for all the models. The k_p/k_s ratio was in the two-digit range, independent of the model used, identifying the peeling reaction as the predominant reaction responsible for cellulose yield loss. The highest ratios were found for Model I, which points to the clear emphasis on the peeling reaction (Haas et al. 1967). Similar k_p/k_s ratios were calculated for models II and III, whereas a significantly higher contribution of alkaline hydrolysis was found for Model II. In Model III, a notable amount of degraded material was attributed to secondary peeling, resulting in a reduction of the hydrolysis reaction rate.

Similar values for the activation energy of the peeling reaction were found for all the models applied. For Model I, the highest activation energy of the stopping reaction was calculated, and the lowest value was calculated using Model III. Applying Model II, E_a = 58.4 kJ/mol was found, and applying Model III, 24.7 kJ/mol were obtained. Despite the lower activation energy of alkaline hydrolysis calculated for Model III, a negligible amount of the cellulose is lost due to the reaction due to a rather low reaction rate (Figure 8).

Influence of oxygen exclusion

Paper 1

For the modelling of cellulose degradation kinetics the experiments were performed under the exclusion of oxygen to prevent undesired side reactions. However, the possibility of oxygen exclusion is difficult to achieve under real process conditions. For the evaluation of the model`s applicability for dissolving pulp steeping, the influence of atmospheric air on cellulose behavior had to be assessed. Therefore, an additional experiment series was performed at 50 °C without air exclusion. The results of the experiments were summarized in a publication (Mozdyniewicz and Sixta 2012).

Enhanced pulp degradation was observed without air removal, as it is shown in Figure 9. Homolytic degradation reactions initiated by the presence of oxygen led to cellulose chain cleavage. The resulting formation of soluble oligomers contributed to the increase in cellulose yield loss and soluble degradation products. However, the effect occurred after one hour – a time period exceeding the treatment times usually applied during viscose production. This fact leads to the conclusion that Model III can be used for estimating cellulose losses during the steeping of dissolving pulp.

In addition to the yield loss, the β-/γ-composition of the resulting lye was investigated. A slight increase in the amount of degradation products was detected. The difference became evident at extended treatment times. The amount of the β-fraction seemed unaffected (Figure 10).

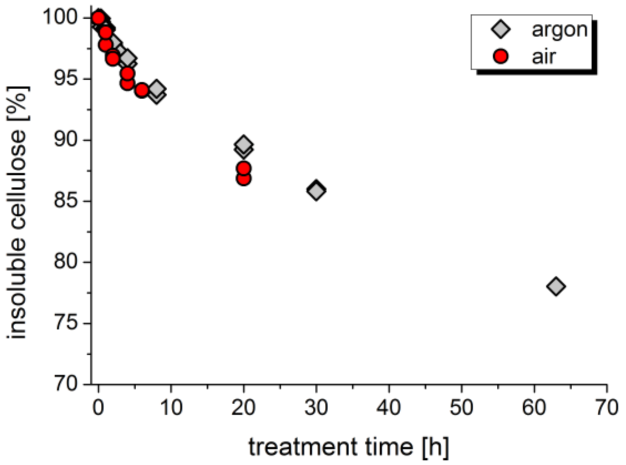

Figure 9 Decrease in cellulose yield with and without air exclusion.

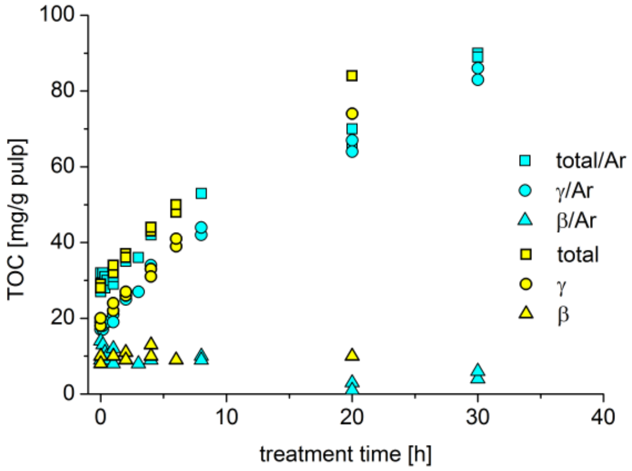

Figure 10 Soluble pulp components present in the lye after alkaline treatment with and without air exclusion obtained by TOC analysis

Changes in pulp crystallinity

The changes in crystallinity with extended treatment time were monitored by NMR measurements of selected samples.

The determination of the single fractions is based on the comparison of peak areas after deconvolution. Inner crystalline, surface crystalline and the disordered fractions of the C-4 atom of the AGU are distinguished. A minimum of the difference of the peak sum and the experimental spectrum is required. The inner crystalline and surface crystalline fractions sum up to the crystallinity index (CrI), indicating the total crystallinity of the cellulose.

Generally, the crystallinity of the samples was found to increase with extended treatment times, and concurrently a marked reduction of the disordered regions was determined. A change of ~17 % occurred after 80 h at 40 °C, and a similar increase was detected after 63 h at 50 °C. A higher reaction temperature (60 °C) resulted in a crystallinity gain of ~11 % after 40 h. At the same time, a distinct reduction of the disordered fraction could be observed for all temperatures. Further, increasing fibril width was observed with increased treatment time. The agglomeration of the cellulose molecules at the accessible crystallite surfaces after removal of the impeding amorphous parts may be a possible explanation.

Different samples treated under the same conditions were measured to ensure the homogeneity of the treatment. In all cases, similar values were obtained for the corresponding residues.

An evaluation of the temperature influence was not possible due to differing initial values. Irregularities of the spectrometer function cannot be ruled out, as long time intervals elapsed between the measurements of the particular series. The complete results are summarized in Table 4.

Table 4 Changes in the crystallinity of the alkaline treated pulp, measured by NMR ©Springer

T [°C]	Treatment time [h]	IC* [%]	SC* [%]	Disordered [%]	CrI* [%]	FW* [nm]
40	0	54.0	15.0	31.0	69.0	4.3
		53.2	14.2	32.6	67.4	4.2
	20	61.7	16.5	21.8	78.2	5.3
	40	62.1	19.5	18.4	81.6	5.4
	80	68.3	17.5	14.3	85.7	6.6
50	0	51.1	11.4	37.5	62.5	4.0
		53.1	13.3	33.6	66.4	4.2
	20	56.7	12.0	31.3	68.7	4.6
		57.2	13.0	29.8	70.2	4.7
	63	65.1	17.8	17.1	82.9	5.9
		63.5	15.5	21.0	79.0	5.6
60	0	57.0	13.8	29.2	70.8	4.7
		55.7	15.8	28.5	71.5	4.5
	10	61.1	17.7	21.3	78.7	5.2
		59.8	16.7	23.5	76.5	5.0
	40	64.1	18.6	17.3	82.7	5.7
		63.4	18.7	17.9	82.1	5.6

** IC…innercrystalline fraction, SC…surface crystalline fraction, CrI…Crystallinity index, FW…Fibril width*

LODP of alkaline treated pulp

Selected alkaline treated pulp samples were subjected to acidic degradation until the Level-off-DP was reached to reveal the influence of the previous reaction conditions. The molar mass distribution and crystallinity of the pulp were investigated. In Figure 11 the molar mass distribution of the samples after the initial steeping, and 20 and 40 hours of alkaline treatment at 60 °C and the corresponding samples at LODP can be found.

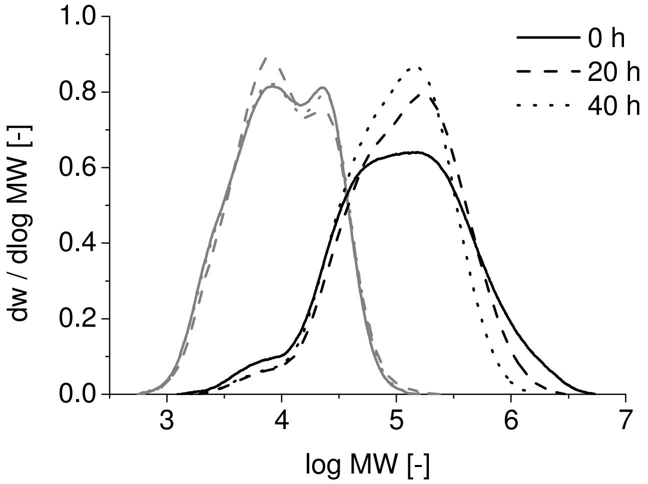

Figure 11 Molar mass distribution of the alkaline treated samples (black lines) and the corresponding Level-off-DP curves (grey lines)

A distinct decrease in the average molar mass occurred after acidic degradation, concurrent with a peak shape change. However, neither a significant difference in average molar mass values nor a clear trend dependent upon the alkaline treatment duration could be detected for the samples. The values of the average molar masses can be found in Table 5.

Table 5 Average molar masses of different alkaline treated samples at LODP

Alkaline treatment time [h]	Mn [kg/mol]	Mw [kg/mol]	Mz [kg/mol]
0	6.41	15.23	28.50
20	6.71	15.89	32.64
40	6.50	15.59	29.85

Despite the similar molar masses, differences in structure could not be ruled out. Therefore, analyses of the crystallinity were performed by NMR spectroscopy. The results of the analyses are summarized in Table 6. Clear trends were found for crystallinity and fibril width changes.

Cellulose degradation under acidic conditions is characterized by an initial phase, when the DP is rapidly reduced. In the theory, a fast degradation of the amorphous regions of the cellulose is assumed (Calvini 2005). The reaction rate is significantly decreased after reaching LODP due to markedly reduced accessibility. Sharples postulated an end-wise degradation pathway at the crystallite edges (Sharples 1957). Based on his hypothesis, the slow reduction of the DP can be explained. The elimination and dissolution of short soluble molecule fragments lead to the preservation of nearly equal average molar mass over extended treatment times. The preferential removal of amorphous cellulose should lead to mostly crystalline residuals with similar composition. Surprisingly, that was not the case for the investigated pulp samples. An increase in the crystallinity was found to occur for longer alkaline treated pulp samples at LODP for all the temperatures applied. Compared to alkaline treated substrates, the increase in crystallinity was not strongly pronounced. The results seem to be in agreement with the theory of the enclosure of amorphous zones between the crystalline regions, which was postulated in previous publications based on FTIR measurements (Salmén and Bergström 2009). Further, the corresponding amount of disordered fractions was preserved in the cellulose during the subsequent acidic treatment. The different swelling time in alkaline solution could lead to an altered enclosure of the amorphous regions between the crystals, changing their accessibility for subsequent hydrolysis.

At the same time, an increase in the fibril width was observed. The aggregation and recrystallization of the cellulose molecules might be a possible explanation for that behavior (Ibbett et al. 2008).

Table 6 Crystallinity of the alkaline treated samples at LODP

T [°C]	Treatment time [h]	IC* [%]	SC* [%]	Disordered [%]	CrI* [%]	FW* [nm]
40	0	66.2	16.3	17.6	82.4	6.1
	40	71.8	15.7	12.5	87.5	7.5
50	0	65.9	14.4	19.7	80.3	6.1
	8	68.8	12.8	18.3	81.7	6.7
	20	73.4	16.2	10.4	89.6	8.0
	30	73.5	16.8	9.7	90.3	8.0
60	0	67.1	13.8	19.1	80.9	6.3
	20	73.8	16.6	9.6	90.4	8.1
	40	75.9	15.9	8.3	91.7	8.8

** IC…innercrystalline fraction, SC…surface crystalline fraction, CrI…crystallinity index, FW…fibril width*

The results of the NMR experiments were confirmed by WAXS for selected samples. Pulps after alkaline treatment at 50 °C were heated with acid until LODP.

Only the cellulose II structure could be found in the investigated pulps. The cellulose was highly ordered with low amorphous background. Average crystallite sizes were calculated using the (1-10), (110), and (020) scatters and applying the Scherrer-formula. The results are shown in Table 7 and the diffractograms are shown in Figure 12.

Table 7 Data obtained by WAXS measurements of alkaline treated samples (50 °C) at LODP

Alkaline treatment time [h]	Crystallinity [%]	k [10^{-2}nm^2]		$D_{(hkl)}$ [nm]	
			(1-10)	(110)	(200)
0	55	2.1	6.0	5.8	5.1
8	60	2.1	6.0	6.0	5.4
30	62	2.4	5.8	6.2	5.6

The differences between the diffractograms of the particular samples were minor, but recognizable, and could be used for the distinction of the particular crystallinity values (Figure 12). The sample after initial hemicellulose removal showed a markedly lower crystallinity than the samples treated for extended time periods. Generally, the values obtained by this method were rather low compared to the NMR results. Therefore, a direct comparison was not expedient; yet similar trends were apparent showing an increase in crystallinity after extended treatment times. In Figure 13, the configuration of the cellulose molecules in a unit cell is shown. The analysis revealed that the distance between the cellulose chains in the axis of the crystal lattice (1-10) remained unchanged. However, an increase in the distance between the parallel chains (200) and between the chains in the unit cell (110) was increased after extended alkaline treatment.

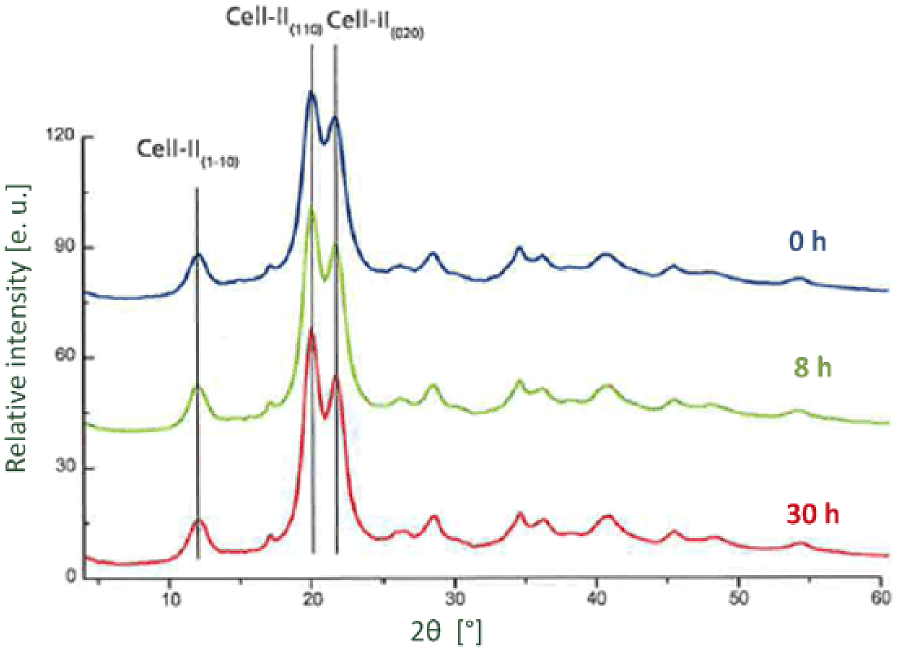

Figure 12 Diffractograms of the alkaline-pretreated pulp samples at LODP

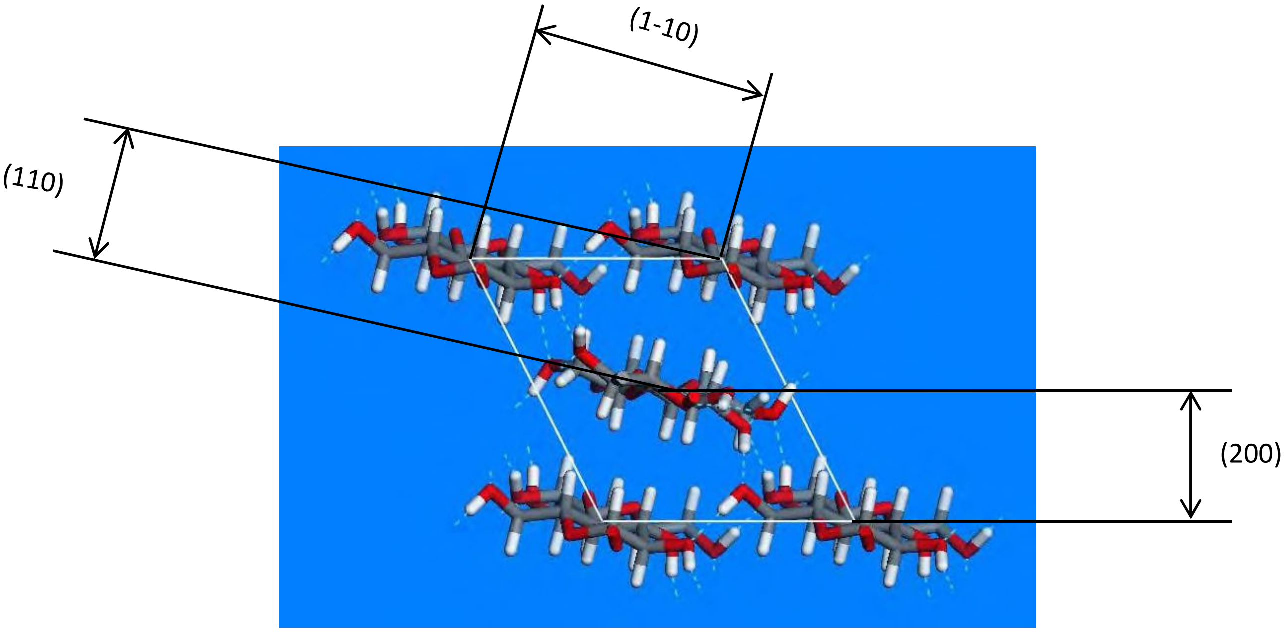

Figure 13 Configuration of the cellulose chains in the cellulose II structure (Eichhorn and Davies 2006)

Generally, the different crystallinity of the LODP samples was found in relation to the previous alkaline treatment duration, independent of the method used. Further, an expansion of the molecules in the 110 direction was observed indicating an influence of the alkaline treatment time on the fibril structure.

Characterization of the β-fraction

Paper 3

The β-fraction was obtained by precipitation from the steeping lye, as shown in the separation scheme in Figure 5. The amount of the fraction formed after a certain time period was detected indirectly by TOC measurements of the lye.

Generally, β-fraction formed a small percentage of the overall organic matter present in the system, including the insoluble cellulose. The amount did not exceed 3 % (w/w) for all temperatures, decreasing with extended treatment times. After maximal time periods for each temperature, yields around 1.5 % were detected. One of the reasons for this is the proceeding degradation of the short chain cellulose present in the precipitated fraction. Its amount is reduced due to the peeling reaction, whereas the xylan is stabilized due to the 4-O-methylglucuronic acid side groups. As xylan formed the main component of the β-fraction obtained, a low degradation rate was detected after a faster initial phase, as it is more stable with regard to the endwise degradation due to the substitution with the 4-O-methylglucuronic acid. This was in agreement with the increase in the relative xylose content with extended treatment times (Figure 14).

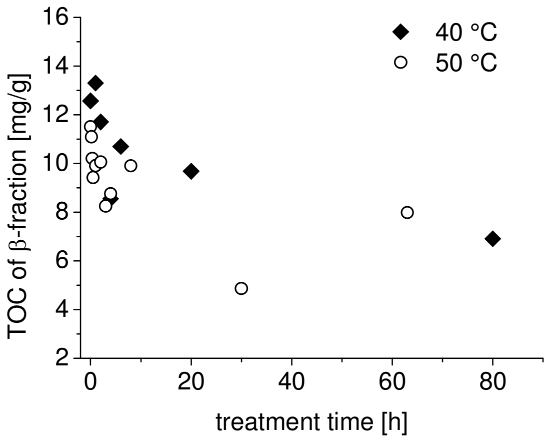

Figure 14 β-fraction formed at 40 and 50 °C obtained by TOC measurements

No influence of the treatment time and temperature of the MMD of the □-fractions could be detected. This may be explained by the precipitation conditions, leading to similar molar mass distributions of the xylans. Generally, an average DP ~ 25 – 30 was determined. In Figure 15, the molar mass distributions of untreated pulp and the cellulose residue after the initial steeping are compared. Additionally, the MMD of the isolated xylan is pictured in the graph. However, the peak area is not standardized for better comparability. Generally, the DP of the isolated xylan was found to be in the range of the xylan initially present in the pulp despite different eluent in the particular GPC systems. The difference between the initial MMD of the pulp and the extracted alkalicellulose provides further confirmation of the accuracy of the data, as a similar molar mass range is covered. All the facts presented above lead to the conclusion, that xylan is removed quantitatively after the initial steeping time and that it is recovered from the lye with slight discrimination of the low MM range (Table 8). The loss most likely occurs due to the washing procedure.

Table 8 Molar masses of the isolated xylan and the calculated peak difference

	Mn [kg/mol]	Mw [kg/mol]
Isolated xylan	3.7	5.5
Calculated difference	3.6	4.4

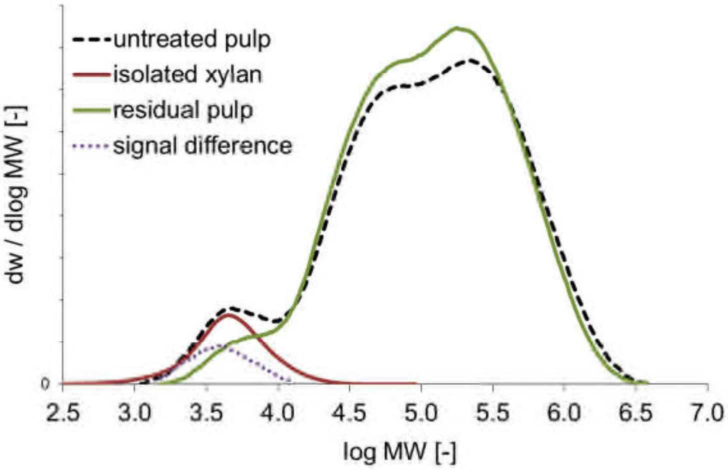

Figure 15 Molar mass distributions of the untreated pulp, pulp after initial steeping and the difference of both MMDs compared to MMD of the isolated xylan (50 °C, after initial steeping time)

The carbohydrate composition of precipitated β-fraction varied with treatment temperature and time. Xylan was identified as the main component and its percentage increased with increased treatment time due to the cellulose degrading peeling reaction. Generally, the amount of cellulose in the samples may occur overestimated, as xylan is incompletely degraded and undergoes undesirable side reactions under total hydrolysis conditions (Vuorinen and Alén 1999).

The analysis of sugar monomers and uronic acids after methanolysis led to the identification of 4-*O*-methylglucuronic acid as a substituent of every 36th xylose unit.

Alkaline degradation products

After the separation of the insoluble cellulose fraction, further investigations of the remaining lye were undertaken. Overall amounts of β- and γ-fractions were obtained by TOC-analysis. In Figure 16 the changes in the fraction concentration with regards to the initial pulp are shown. A significant increase of the γ-fraction with extended treatment times was determined, independent of the temperature applied. A low percentage of the β-fraction in relation to total amount of degradation products led to the assumption that TOC formation is largely attributable to insoluble cellulose degradation due to the peeling reaction.

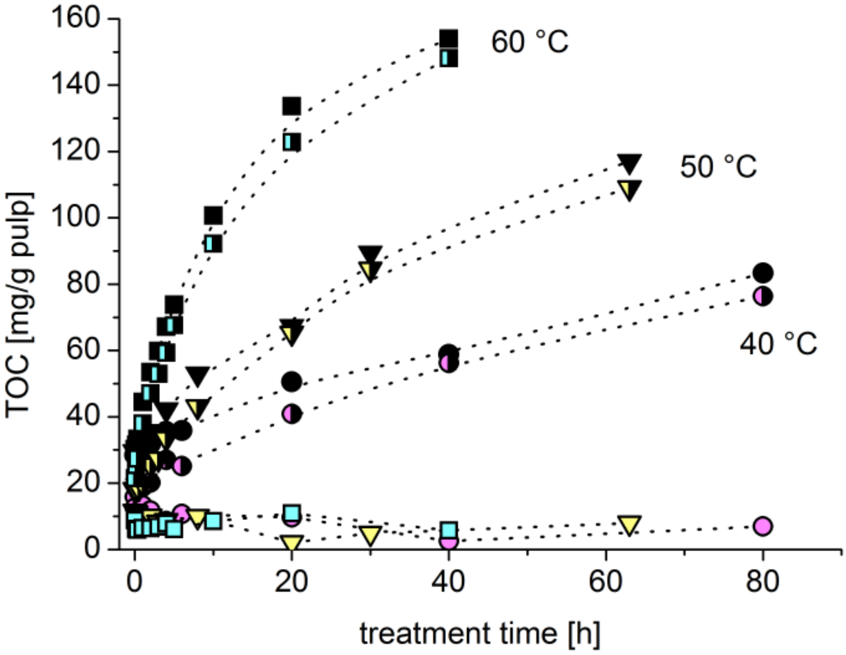

Figure 16 Total organic carbon content of the separate fractions after treatments at 40 (filled circle), 50 (filled inverted triangle) and 60 °C (filled square). Full symbols represent the total amount, half-filled symbols represent the γ-fraction and empty symbols represent the β-fraction ©Springer

Thirteen different hydroxy acids were detected as pulp degradation products (Figure 17). Most of them have already been reported in previous publications (Knill and Kennedy 2003). α- and β-glucoisosaccharinic acids (XII a, b) were identified as the main degradation products, independent of the temperature and treatment time. Lactic acid (II) was found in considerable amounts in all the investigated samples. Together with glycolic acid (I), it frequently occurs as a typical cellulose degradation product. Xyloisosaccharinic acid (XIII) was found in all the analyzed samples and can be clearly attributed to the xylan present in the pulp, as a degradation mechanism similar to cellulose was postulated for the formation (Niemelä 1990a).

Most of the hydroxy acids found in the γ-fraction were identified as cellulose and hemicellulose degradation products and their occurrence had been described in several publications (Aspinall et al. 1961; Niemelä 1990b; Niemelä and Sjöström 1986b; Knill and Kennedy 2003). Some of the acids, not identified before, were found in minor concentrations in few samples.

Generally, a higher quantity of degradation products was formed with increasing reaction temperature. Most of the compounds present in the solution were formed from cellulose due to its quantity within the reaction mixture. However, the sum of the detected hydroxy acids was significantly lower than the corresponding TOC-content of the γ-fraction. At 40 °C the maximum amount was equivalent to 31 % of the TOC. At higher temperatures, values around 50 % were achieved at the most. Possible reasons for the incomplete identification could be the analyte concentrations below the detection limit, unidentified components, and losses due to sulphate removal.

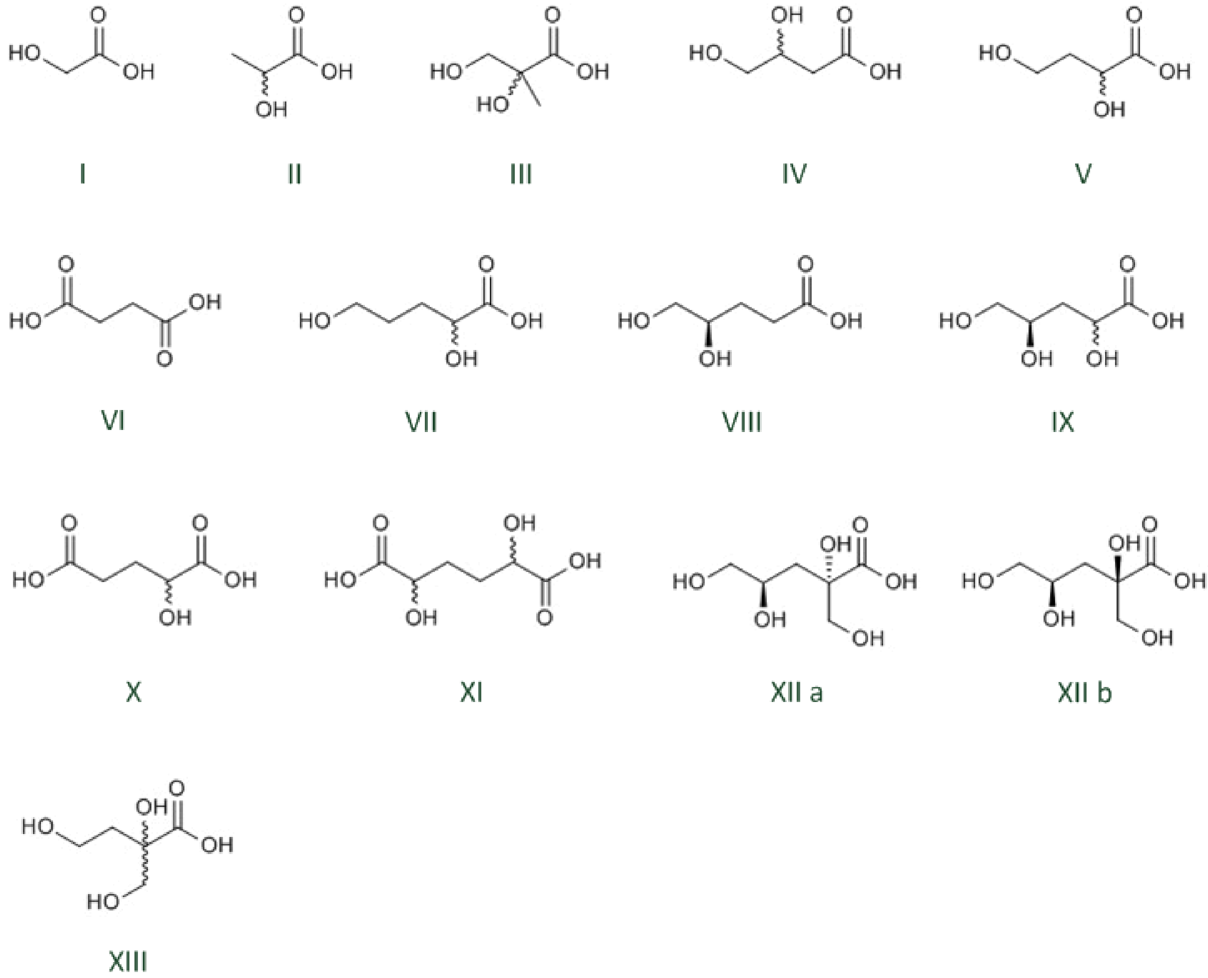

Figure 17 Structures of the alkaline degradation products identified in the liquid: glycolic acid (I), lactic acid (II), 2-methylglyceric acid (III), 2-deoxytetronic acid (IV), 3-deoxytetronic acid (V), succinic acid (VI), 2,5-dihydroxypentanoic acid (VII), 4,5-dihydroxypentanoic acid (VIII), 3-deoxy-threo/erythro-pentonic acid (IX), 2-hydroxyglutaric acid (X), 3,4- dideoxyhexaric acid (XI), a-glucoisosaccharinic acid (XII a) bglucoisosaccharinic acid (XII b) and xyloisosaccharinic acid (XIII). Stereochemistry referring to Knill and Kennedy (2003); ©Springer

Acidic fiber treatment

Paper 4

Degradation kinetics

The behavior of viscose fibers with different intrinsic viscosity and hemicellulose content under long-term treatment in a spinning bath was evaluated. Four fiber types with the properties shown in Table 2 and Figure 6 were used. The experiments were carried out at different temperatures (40, 50, and 60 °C) with residence times up to 292 hours.

A model illustrating the reduction of DP was developed, based on preceding work by Calvini (Calvini 2012). Further, the formation of degradation products was monitored to enable the quantification of TOC enrichment in the acidic medium.

In previous publications, three categories of cellulosic bonds were distinguished, characterized by their chain scission reaction rates. The existence of weak links was postulated, characterized by the initial rapid decrease of DP. Distinctly slower cleavage of the bonds occurred in the amorphous regions of the cellulose. Finally, the hydrolysis reached the crystalline regions, and the reaction rate apparently stagnated, as the degradation proceeded only at the edges of the crystallites (Figure 18).

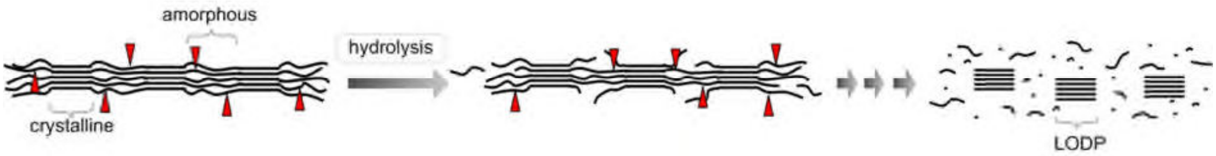

Figure 18 A simplified illustration of cellulose hydrolysis

Degradation kinetics was modelled by fitting the experimental data obtained after acidic fiber treatment. After analysis, the contribution of cellulose molecules within the crystallites was considered negligible, due to a very slow reaction rate. This approach was supported by SEC analyses. A significant difference between the MMD at LODP and the longest applied treatment times was determined, indicating a considerable amount of non-crystalline fraction accessible for hydrolysis for all the experimental conditions. Further, similar behavior of the MMD modification was found for all temperatures, confirming the temperature dependence of the reaction rate, but not of the pathway. The presence of hemicellulose in the fibers did not influence the MMD transformations. The MMD changes in fibers B after varying treatment times at 40 and 60 °C and at LODP are illustrated in Figure 19.

Weak and amorphous links were taken into account for the system description. The changes in DP with proceeding degradation time could be described by following equation:

$$DP = \frac{DP_0}{M_0\left(1-e^{-k_1 t}\right)+W_0\left(1-e^{-k_2 t}\right)+1} \qquad \text{IX}$$

where DP was the degree of polymerization at time t, and $DP_0$is the initial degree of polymerization.

Considering the number of scissions per molecule the remodeled equation was as follows:

$$\frac{DP_0}{DP} - 1 = M_0\left(1 - e^{k_1 t}\right) + W_0\left(1 - e^{k_2 t}\right) \qquad \text{X}$$

Level-off DP analyses of the fibers were performed to obtain the initial amounts of both, slow degrading and fast degrading amorphous bonds. Calvini suggested the Level-off-DP value to be a crucial parameter for the modeling of cellulose hydrolysis, due to the significant influence of crystalline amount on the total degradation rate (Calvini 2005). In our case, approximately equal values were obtained for all fiber types, indicating different amounts of the amorphous material dependent upon the cellulose chain length.

Increasing reaction rates were determined with enhanced temperature for all fiber types. Using the Arrhenius equation, frequency factors and activation energies were determined, differing slightly from previously reported values due to deviations in the experimental setup (Garves 1996; Mozdyniewicz et al. 2015).

Changes of fiber properties

Higher fractions of the weak bonds were found in fibers with higher initial viscosity (B and D), coinciding with the lower activation energy values of the fast degradation. However, no evidence was found for a faster degradation of hemicellulose-rich fibers; though, increased hemicellulose loss with proceeding treatment time was indicated by carbohydrate analysis and by the amount of soluble degradation products formed.

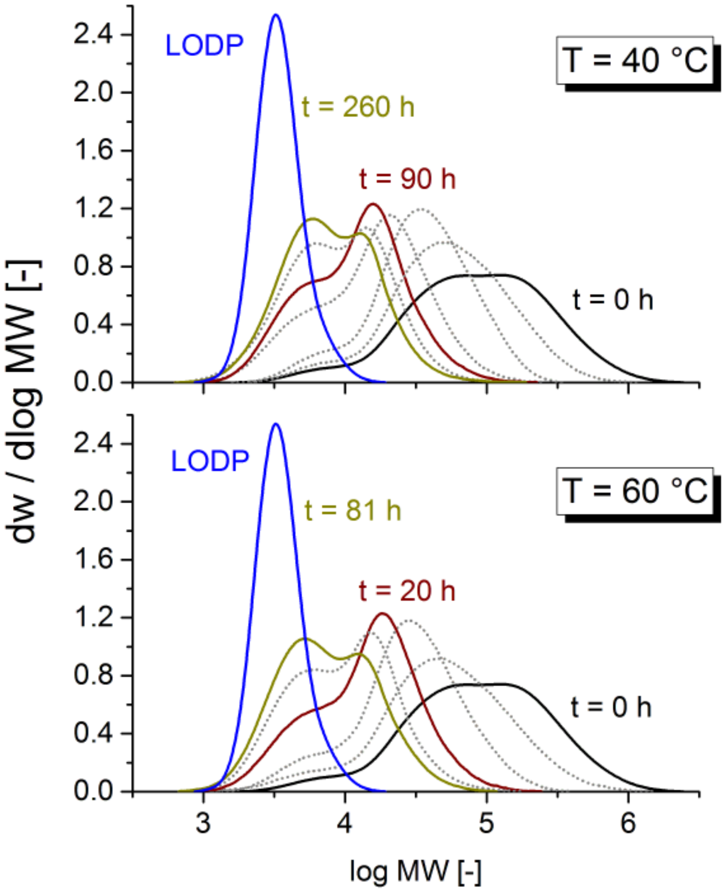

Figure 19 Changes in the MMD with treatment time

The observed changes in crystallinity indicated a removal of the amorphous material with proceeding acidic treatment. However, the results were not confirmed by gravimetric analysis, as negligible yield losses were determined. Recrystallization was a possible explanation for the behavior. The formation of crystallites in the amorphous sections is initially inhibited due to the rigid surrounding crystalline structures. Chain scissions in the amorphous regions due to acid hydrolysis release the molecule fragments enabling an agglomeration on the crystallite surface (Ibbett et al. 2008).

Conclusion

An established model was successfully adapted for the description of cellulose degradation in viscose fibers, considering different initial DP and hemicellulose content. The contribution of crystalline regions to cellulose degradation was found to be negligible for the applied conditions, due to predominant amorphous fraction, even after extended treatment times. The existence of two kinds of bonds in the amorphous regions was postulated: faster and normal degrading. Activation energies and frequency factors were determined for both types. Hemicellulose loss occurred independently of the initial concentration in the fibers and proceeded faster at higher temperatures. Further, a higher concentration of TOC in the residual spinning bath was found after the treatment of hemi-rich fibers. Therefore, one should keep in mind that the production of the novel fiber type using hemicellulose-rich waste lye may have consequences for the waste water treatment. The removal of the extent undesired organic compounds from the spinning bath is necessary to guarantee unchanging product quality. As an alternative, hemicellulose-containing lye with a lower concentration of degradation products should be used.

Evaluation of viscose spinning conditions

A reduced factorial design was chosen to evaluate the influence of four relevant parameters on the viscosity of the final fibers and the TOC formation in the spinning bath. The factors comprised the temperature and acidity of the spinning bath in an industrial range as well as the DP of the alkali cellulose after aging and the presence of hemicellulose.

The analysis of the results was performed using the software Design Expert® 9. It should be noted, however, that the linear dependencies of the parameters were assumed in the models. Within the narrow conditions applied it was initially considered to be a suitable approach.

In the first case, the influence of the variables on the viscosity change was evaluated. Therefore, all the available data were considered. A and D were the significant model terms. In Table 9, the effects of all the variables on the response values are listed. The initial viscosity of the cellulose in the fibers and the addition of hemicellulose seem to have the greatest positive effect on the viscosity difference of the fibers and TOC formation in the spinning bath and aftertreatment. In conclusion, the addition of hemicellulose leads to a decrease in viscosity, which is an obvious consequence due to a markedly lower DP.

Table 9 Evaluation of the particular effects on the response values including the hemicellulose influence

Response	A (η_{AC}) [ml/g]	B (T) [°C]	C (Acid) [g/l]	D (HC) [%]	R^2
$\Delta\eta$	10.0	n. s.	n. s.	14.08	0.9729

n. s. not significant

The following equation was obtained for the estimation of fiber viscosity:

$$\Delta\eta = -0.26441 + 0.039984 \times \eta_{AC} - 1.14062 \times HC$$

where η_{AC} is the intrinsic viscosity of the cellulose used for the viscose dope production and HC the hemicellulose content in the fibers.

For TOC formation in the spinning bath, the factors A, D and AD were significant model terms. Concerning η_{AC}, a positive effect was found concerning the spinning bath, but a negative overall effect (Table 10). Higher chain length seems to result in a lower amount of soluble degradation products.

Table 10 Evaluation of the particular effects on the TOC formation

Response	A (η_{AC}) [ml/g]	B (T) [°C]	C (Acid) [g/l]	D (HC) [%]	AD	R²
TOC (SB)	5.7	n. s.	n. s.	13.9	-3.6	0.9941
TOC (Σ)	-17.0	n.s.	n.s.	111.7	-11.2	0.9968

n.s. not significant

The influence of the temperature was quite small. Further, the addition of hemicellulose resulted in an increased release of organic compounds during spinning. The influence of η_{AC} and the hemicellulose content is shown in Figure 20.

The formation of TOC in the spinning bath can be described by the equation below:

$$\text{TOC (SB)} = 2.58946 - 5.98658 \times 10^{-3} \times \eta_{AC} + 1.81281 \times \text{HC} - 2.53714 \times 10^{-3} \times \eta_{AC} \times \text{HC}$$

The addition of hemicellulose had a great impact on the final average viscosity due to a considerably lower chain length. Additionally, the variation of the xylan content from 0.7 % to 12.5 % by far exceeded the range of the industrial man-made cellulosic fibers available at the market. To take account of this fact, a second approach was performed: an analysis of the data set without hemicellulose. Instead of η (fiber), the amount of chain scissions was chosen as a response value due to its independence of the initial η_{AC}.

The entire TOC amount formed during spinning and the subsequent after-treatment is estimated by the following equation:

$$\text{TOC } (\Sigma) = 4.06138 - 0.014126 \times \eta_{AC} + 11.16910 \times \text{HC} - 8.20293 \times 10^{-3} \times \eta_{AC} \times \text{HC}$$

Excluding the dominant effect of hemicellulose concentration, a clearer and more precise picture was visible. Only term A was found significant for the amount of chain scissions. The appearing effects are shown in Table 11. Increasing η_{AC} and increased the number of scissions. Longer cellulose chains contain more amorphous regions resulting in higher accessibility.

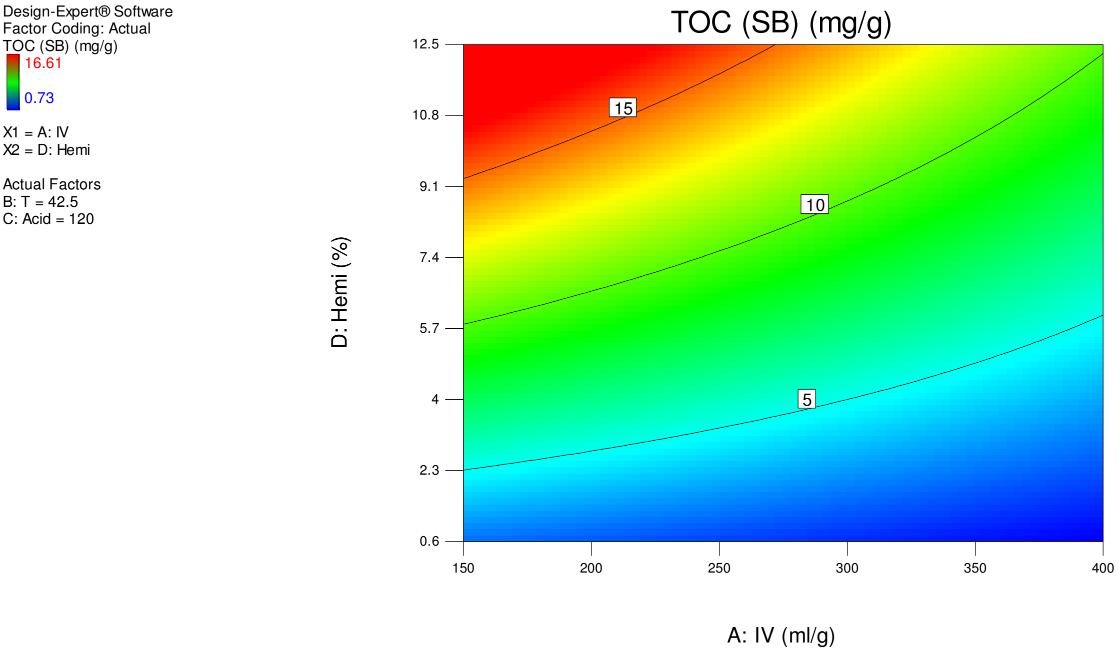

Figure 20 Influence of the hemicellulose content and the initial intrinsic viscosity on the TOC content in the spinning bath

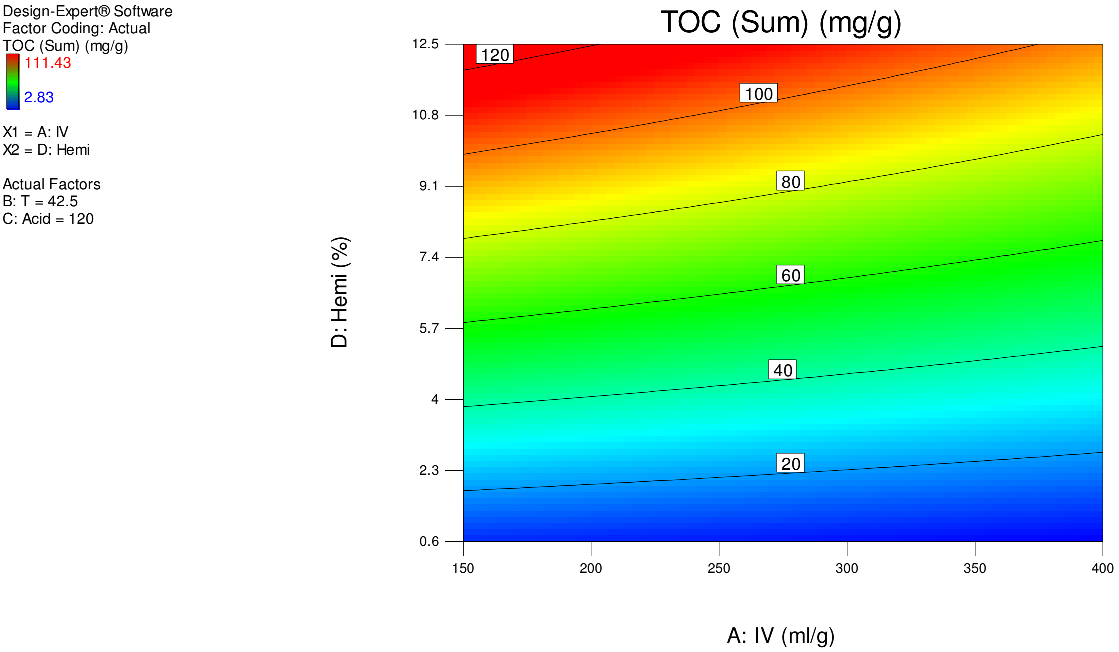

Figure 21 Influence of hemicellulose content and the initial intrinsic viscosity on the entire TOC content

Table 11 Evaluation of the particular effect on the response values excluding the hemicellulose

Response	A (η_{AC}) [ml/g]	B (T) [°C]	C (Acid) [g/l]	R²
CS	0.17	n. s.	n. s.	0.9137

Generally, the amount of chain scissions may be estimated using following equation:

$$CS = -0.24755 - 1.13418 \times 10^{-3} \times \eta_{AC} + 2.60106 \times 10^{-3} \times T + 6.45767 \times 10^{-4} \times Acid - 1.03175 \times 10^{-5} \times \eta_{AC} \times T$$

with CS representing the amount of chain scissions

Initial intrinsic viscosity was found to be significant for TOC formation in a spinning bath (Table 12).

Similar to the model including hemicellulose, the negative effects of η_{AC} were found for TOC (SB) and TOC (Σ). In the case of TOC (Σ), more effects had to be taken into account to obtain a reasonable R² value for the model. The temperature of the spinning bath had a positive effect on TOC (Σ) formation, while the influence on TOC in the spinning bath was not significant.

Table 12 Influence of the particular factors on TOC formation

Response	A (η_{AC}) [ml/g]	B (T) [°C]	C (Acid) [g/l]	AC	BC	R²
TOC (SB)	-2.28	n. s.	n. s.	n. s.	n. s.	0.8751
TOC (Σ)	-13.2	8.28	n. s.	7.5	-9.3	0.9673

The following equations were obtained for TOC (SB) and TOC (Σ):

$$TOC\ (SB) = -4.27426 - 9.11422 \times 10^{-3} \times \eta_{AC} + 0.17275 \times T + 0.067635 \times Acid - 1.36306 \times 10^{-3} \times T \times Acid$$

$$\mathrm{TOC}\ (\Sigma) = -97.20808 + 0.14788 \times \eta_{AC} + 3.80227 \times T + 0.74131 \times \mathit{Acid} - 7.65813 \times 10^{-3} \times \eta_{AC} \times T - 1.15554 \times 10^{-3} \times \eta_{AC} \times \mathit{Acid} - 0.027191 \times T \times \mathit{Acid} - 5.51172 \times 10^{-5} \times \eta_{AC} \times T \times \mathit{Acid}$$

Generally, the predominating effect of the initial intrinsic viscosity is visible after the analysis of the experiments without hemicellulose addition. The variation range of the chain length was quite large compared to the other values therefore, a detectable effect was found.

Conclusion

The short residence time in the spinning bath was a challenge for the investigation, yet the statistical evaluation enabled the identification of the trends concerning TOC formation and final intrinsic viscosity.

The concentration of hemicellulose in the dissolving lye used for the production of fibers was identified as the predominating factor during the regeneration of hemi-enriched viscose. The significant increase of the released TOC provides challenges in removal of the undesired organic compounds.

The analysis of the data set without added hemicellulose showed that the initial intrinsic viscosity had an influence on TOC formation in the spinning bath. With increasing cellulose chain length, TOC amount decreased.

For further optimization, experiments in a wider parameter range would be necessary due to the minor significance of the factors within the investigated boundaries. However, the limitations in terms of feasibility did not enable a more precise study.

Xylan isolation

Two different extraction methods were used for the isolation of xylan, as the varying properties of the solvents used were assumed to have an influence on the extracted substrates. The DMSO-method was used without further modifications, whereas for the Nitren-method an optimization of extraction conditions was realized on the basis of previous results (Janzon et al. 2006). High xylose content in the extracted phase with concurrent low cellulose loss of the residual pulp was desired. The yields did not play a decisive role in the optimization step.

For the initial experiments, beech brown stock was used, on the one hand due to availability, and on the other hand, due to a higher xylan content compared to final bleached pulp. Further, the considerable amount of lignin present in the substrate might have required further method adaptation. In Table 13 the results of the initial experiments are shown. A significant reduction of xylan in the original substrate occurred. However, the high cellulose content was extracted concurrently and could be found in the xylan fraction. Therefore, more suitable extraction conditions had to be found.

Table 13 Residuals after extraction with 5 % Nitren (L/P 10:1) at room temperature (1 h)

Sample	Glc [%ATS]	Xyl [%ATS]	Man [%ATS]	Rha [%ATS]	Σ [%ATS]
BBS	88.2	5.3	0.9	0.1	94.4
BBS (residual)	85.6	1.1	0.9	0.0	87.6
Xylan	61.3	22.0	0.1	0.0	85.5

The processability of the L/P ratio of 10:1 was not satisfactory; therefore, a higher ratio was chosen for the following experiments. Further, a lower Nitren concentration was applied to minimize cellulose extraction. The results are shown in Table 14. A slightly lower xylan amount was extracted using lower solvent concentration; however, satisfactory xylan purity was obtained with the conditions applied. Therefore, the conditions were used for further extractions.

Table 14 Residuals after extraction with 2.5 % Nitren (L/P 15:1) at room temperature (1h)

Sample	Glc [%]ATS]	Xyl [%ATS]	Man [%ATS]	Rha [%ATS]	Σ [%ATS]
BBS	88.2	5.3	0.9	0.1	94.4
BBS (residual)	89.1	1.9	0.9	0.0	96.1
Xylan	2.5	79.1	0.0	0.0	81.6

Extraction yields

For the determination of the extraction yield, the ratio of the residual xylan fraction mass and the initial xylan content in the substrate was calculated. The results are shown in Table 15. Generally, distinct results were obtained by both extraction methods. For most of the Nitren extracts, yields between 30 and 50 % were found, slightly varying dependent upon the raw material. With exception of beech wood xylan, the relative extracted amount decreased with progressing refining steps.

A similar decrease of the yields was found after the DMSO method. However, in both species, beech and eucalyptus, exceptionally high amounts were obtained by the extraction of delignified wood. Comparable amounts were extracted from the pulps.

Generally, higher accessibility of wood xylan may be assumed after comparison of the results. Degradation of the accessible xylan under harsh pulping conditions seems to occur, independent of the pulping process applied. However, residual lignin content may be responsible as well for the distinct deviation.

Table 15 Extraction yields based on the xylan content in the initial substrates

	Extraction yield (by Nitren) [%]	Extraction yield (by DMSO) [%]
BW	9.27	98.6
BBS	51.6	28.3
BSP	41.3	24.9
EW	50.0	95.2
EBO	39.0	34.9
EKP	32.2	31.3

In summary, sufficient extraction yields were found in most raw materials used, enabling further characterization.

Carbohydrate composition

Xylans of a high degree of purity were obtained by both isolation methods used. Slightly higher cellulose content was found in xylans from final bleached beech pulp (Figure 22). An amount of approximately 10 % was present in the DMSO-substrate, the application of the Nitren method resulted in approximately 4 % residual cellulose. The decreased solvent selectivity due to the particularly low xylan content in the pulp led to an undesired dissolution and isolation of cellulose.

The determination of carbohydrate composition after total hydrolysis resulted in yields < 100 % for all xylans, irrespective of the isolation method. A possible explanation for this fact is the occurrence of side reactions under sulphuric acid hydrolysis (Vuorinen and Alén 1999). Further, the slightly brown color of the samples indicated the presence of residual lignin content, especially in the wood originated xylans. More detailed lignin analyses were not performed due to relatively low sample amounts.

Xylan purification by fractionation

The aim to achieve the highest possible xylan content in the isolated fractions could not be achieved for all the samples straight from the Nitren extraction procedure. The results were in accordance with those of a recent study, revising the previously described high selectivity of Nitren for xylan extraction (Dos Santos et al. 2013). Therefore, attempts were made to eliminate the residual cellulose content due to the fractionation by changes in the pH (personal communication with Dos Santos, N.). The xylan-containing solution was first adjusted to pH 7 by the addition of formic acid. An initial precipitation of a cellulose-enriched fraction was expected as a result of the procedure. Xylan was supposed to remain dissolved until a pH of 3 was reached. However, the fractionation did not result in appreciable improvement. In Table 16 the properties of the fractions obtained after the extraction of the unbleached beech pulp are shown.

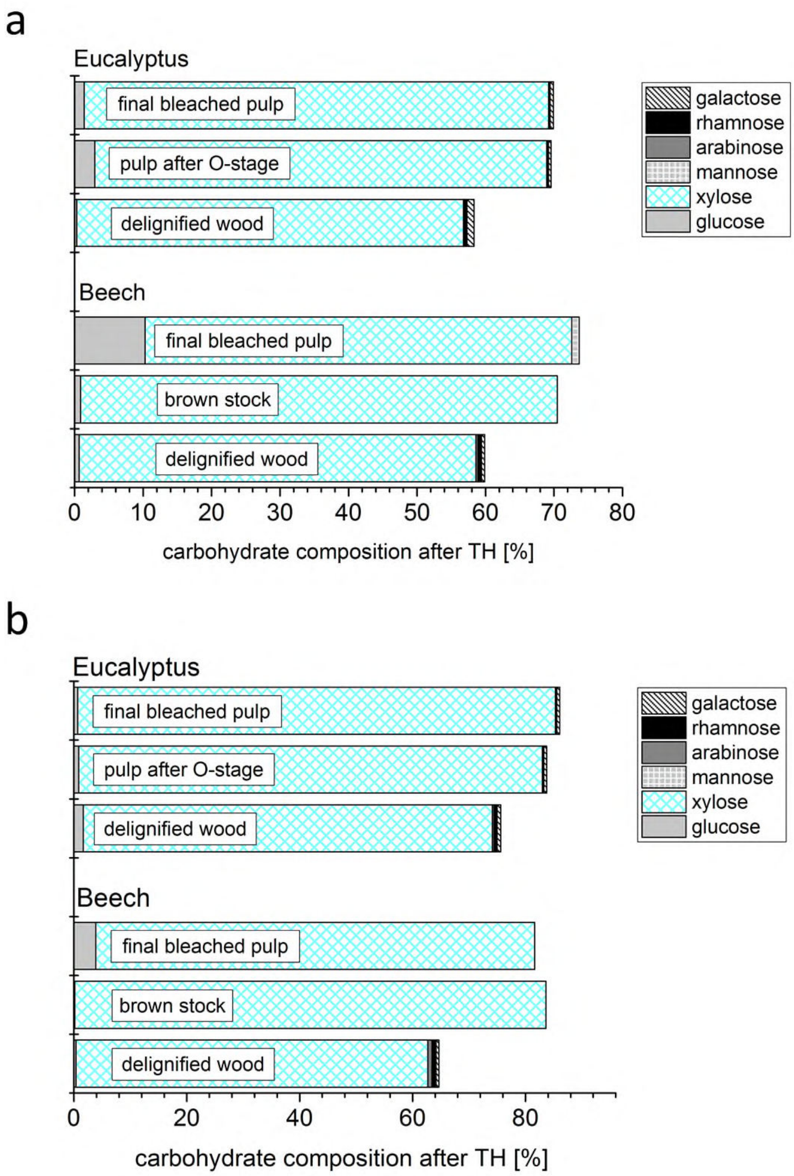

Figure 22 Carbohydrate composition of the isolated xylans by DMSO (a) and 2.5 % Nitren (b)

The average molar masses of both samples were quite similar and same DP values were obtained after calculation. Xylan was found to be the main component in both fractions. However, the carbohydrate yield of the first sample was distinctly lower, which indicates considerable residual lignin content further confirmed by a pronounced color difference (Figure 23).

Table 16 Properties of the different pH fractions from beech unbleached pulp

Fraction	Xylan [%]	Glucan [%]	Σ [%]	Mn [kgmol-1]	Mw [kgmol-1]	PDI	DP
pH 7	76.5	0.3	76.8	4.4	4.5	1	33
pH 3	98.2	0.7	98.9	4.3	4.4	1	33

The role of the lignin could not be clearly determined. It remained unknown whether it was separately dissolved in Nitren and concurrently precipitated due to a decrease in pH or bound at the xylan from the beginning, forming LCCs.

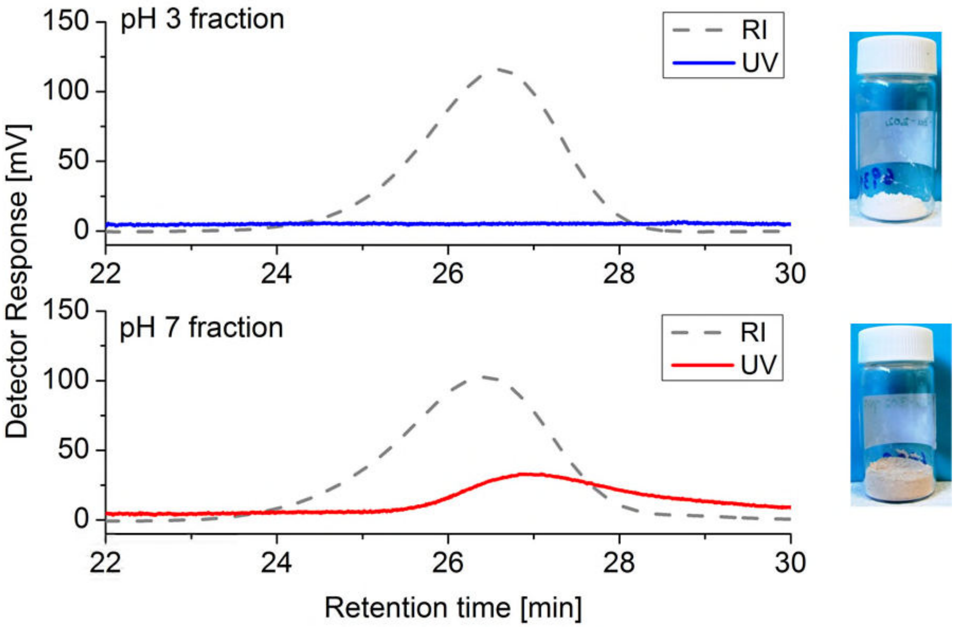

Figure 23 Fractions obtained by different pH values after Nitren treatment of unbleached pulp

Molar mass distribution after Nitren-extraction

Material loss during the washing procedure could not be ruled out, as in some cases a turbid supernatant was obtained after centrifugation. Therefore, experiments were performed to reveal a potential discrimination of a particular molar mass fraction due to incomplete sedimentation. For this purpose, selected samples were analyzed directly after the extraction procedure. After extraction by 2.5 % Nitren solution, samples were directly analyzed with the standard SEC system to compare the MMDs with the precipitated and subsequently dissolved xylans. The results of the analyses are shown in Figure 24.

Looking at the conventionally analyzed samples, differences in the molar mass distribution due to varying pulping and bleaching conditions can clearly be seen. A gradual decrease in the average molar mass of the eucalyptus xylans was evidence of a minor reduction after pulping and bleaching, as the preservation of the xylan is desired during paper pulp production. In contrast, the average molar mass of the beech xylans was reduced more radically during dissolving pulp production. Hemicellulose is strongly degraded under sulphite pulping conditions; practically no difference was detectable between the xylans isolated from brown stock and final bleached pulp.

Only slight differences in average molar masses were found between the precipitated and directly analyzed samples. The same trends were observed regarding the xylan behavior during pulp production processes. A clear influence of the solvent on the peak form was visible. A considerable peak broadening compared to repeatedly dissolved samples prevented the precise detection of the average molar mass. Particularly the MMDs of the low molar mass beech xylans were shifted to lower values when using Nitren as a solvent. Generally, comparable results were obtained with both methods, especially concerning the trends of the chain shortening within the process.

The discrimination of a certain low molar mass fraction could not be excluded by evaluation of the data. The directly analyzed samples of beech brown stock and pulp xylans showed significantly lower average molar masses, compared to the repeatedly dissolved substrates. This was not the case for the higher molecular eucalyptus xylans. Further evidence for the limitation of sedimentation of low molar mass xylans is the similarity of the MMDs of re-dissolved beech brown stock and pulp samples. Parts may be separated during the washing procedure, leading to an apparent increase in the average molar mass. However, the effect may result from varying solvent properties as well. The possible solvent influence on the sample retention may further be an explanation for peak broadening. The greater difference between the wood and pulp xylans may contribute as well to a high extent to peak shift due to the longer retention times of smaller molecules.

Generally, similar trends of xylan degradation due to pulping and bleaching were found, independent of the isolation method. Particularly the high molar mass eucalyptus xylans and beech wood xylans showed a good correlation of the values. However, a significant peak broadening was determined for the directly analyzed samples.

Uronic acid content

Methanolysis was applied to demonstrate the differences in uronic acid content dependent on the production stage and isolating agent. 4-O-methylglucuronic acid was found in all samples in varying concentrations. The amount present in the beech wood xylans obtained by DMSO was in good agreement with the values present in the literature, confirming the analysis results (Teleman et al. 2002).

Generally, similar substitution patterns were found for both wood species over the course of pulping and bleaching, independent of the isolation method (Figure 25). The concentration of 4-O-methylglucuronic acid decreased in the initial phase and increased again due to the bleaching step. The degradation of unsubstituted xylan after cleavage under the strong oxidative conditions might be a possible explanation for the results.

Galacturonic acid (GalA) and glucuronic acid (GlcA) were only found in the wood isolated xylans. Galacturonic acid was present in higher amount in the xylans obtained after Nitren treatment. Fractional amounts were found in the DMSO samples. Therefore, galacturonic acid seems to be contained in xylan fractions not accessible to that solvent. Traces of glucuronic acid were found in DMSO-extracted wood xylans in similar concentrations. The accurate contents can be found in Table 17.

Table 17 Concentration of galacturonic (GalA) and glucuronic (GlcA) acids in wood xylans

	GalA [%]	GlcA [%]
Beech wood xylan (DMSO)	0.62	0.14
Beech wood xylan (Nitren)	5.47	-
Eucalyptus wood xylan (DMSO)	0.36	(< 0.1)
Eucalyptus wood xylan (Nitren)	7.69	-

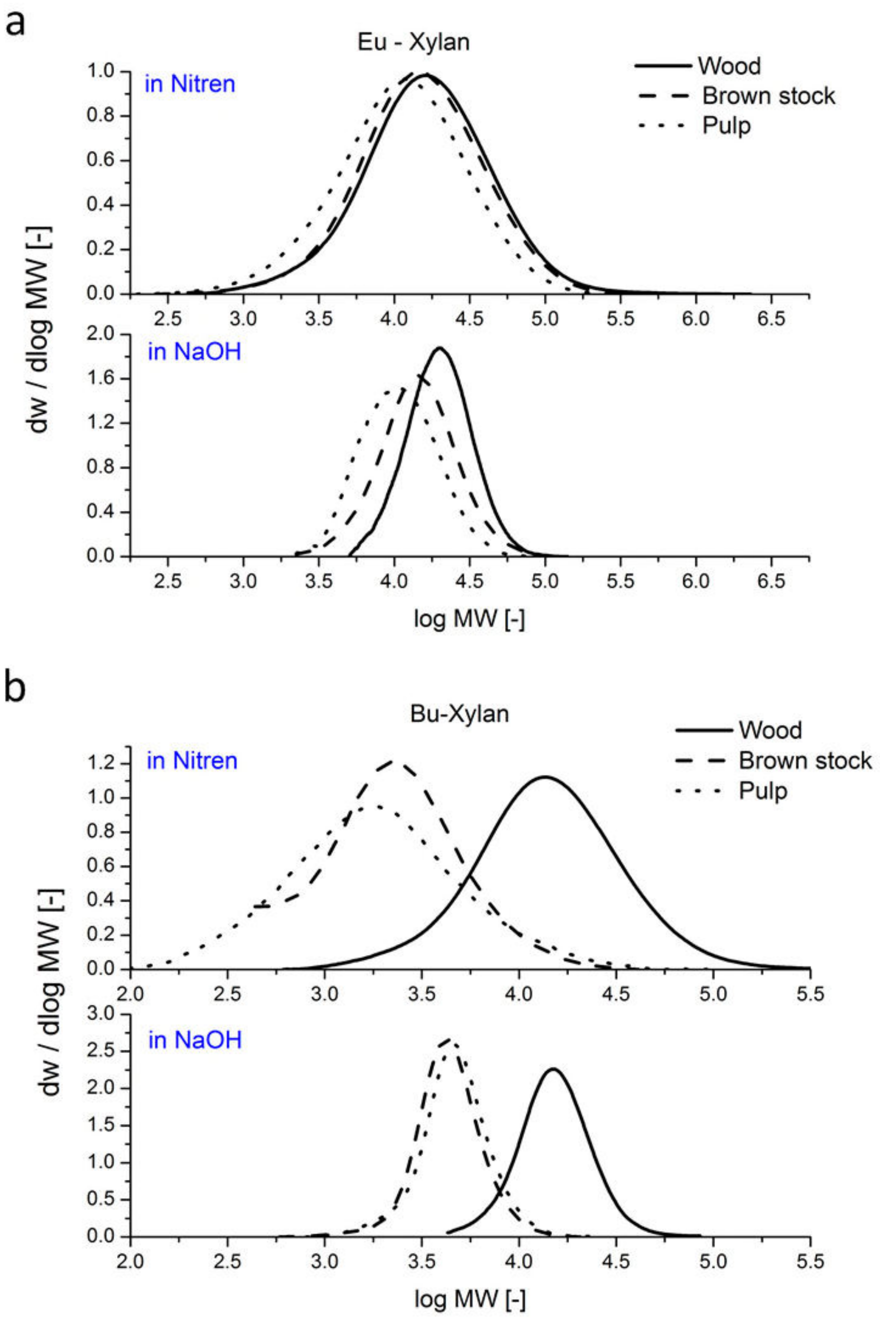

Figure 24 Molar mass distributions of xylans obtained by extraction with 2.5 % Nitren. A comparison between xylan in solution and after precipitation and dissolution. Eucalyptus substrates (a) and beech substrates (b)

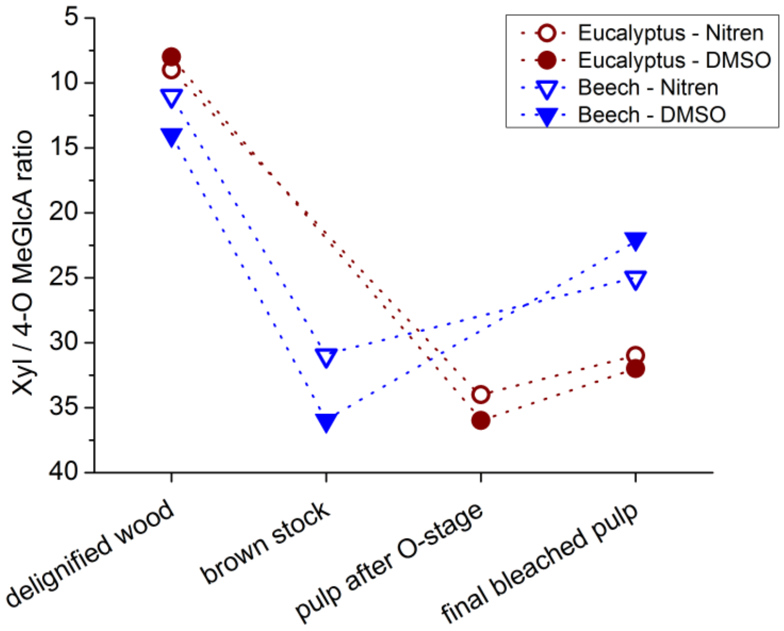

Figure 25 Concentration of 4-O-methylglucuronic acid in the isolated xylans

Conclusion

Xylans of high purity were obtained from beech and eucalyptus wood and pulps by both extraction methods applied. Sufficient yields were obtained, decreasing after pulping and bleaching steps due to the reduction of xylan amount within the process steps. This means that xylan extraction was feasible in every production stage despite the quite different properties of the solvents used. The optimum isolation stage, however, depends on the required characteristics and the intended use of the xylan. Generally, the extraction is most effective in a stage where a high amount of the hemicellulose is present. Further, a higher selectivity of the solvent may be ensured. However, an incomplete removal from the pulp might be an advantage, as this prevents hornification, which is responsible for insufficient pulp reactivity (Oksanen et al. 1997).

An additional decisive factor for an effective separation is the difference between the molar masses of the cellulosic and hemicellulosic fractions of the pulp. In the case of the eucalyptus wood and Kraft pulps, only slight changes in the MMD of xylan during the production were detected. Together with a striking molar mass difference in comparison with the cellulosic fraction, ideal separating conditions were found for all the substrates. In association with the high hemicellulose contents for all substrate types, the extraction seems profitable. Hemicellulose removal further enables the conversion of paper grade to dissolving pulp in a relatively easy way and has already been carried out by pulp producers (Schild et al. 2010).

A different behavior was found for the beech substrates, as they were obtained by dissolving pulp production. The distinction between the MMDs of cellulose and xylan was less pronounced, as both fractions were degraded during the sulphite cooking and the subsequent bleaching steps. Further, a significant reduction of the hemicellulose amount in the course of dissolving pulp production is achieved. Therefore, isolation in the early stage should be considered, however, at the expense of decreased accessibility.

The use of DMSO is advantageous for the isolation of water soluble xylans; however, the chemicals consuming and therefore costly precipitation procedure excludes its feasibility for industrial production, unless a beneficial recycling concept is found. Isolation by an established process and subsequent derivatization may be a possible alternative.

The direct isolation of wood xylan by both solvents resulted in a high content of 4-O-methylglucuronic acid. For highly substituted hemicellulose, the extraction of wood should be preferred. 4-O-methylglucuronic acid may be isolated after xylan hydrolysis, similar to galacturonic acid, which was present in considerable amounts in both wood xylans extracted by Nitren. Nonetheless, xylan may be converted to monomers due to hydrolysis and may be used as a basic material in biotechnology, culture broth for microorganisms or for the production of fine chemicals.

Future Outlook

The technology of cellulosic fiber production by the viscose process has been successfully applied for over a century which made it possible to produce high quality fibers to meet the growing demand. However, it is foreseeable that it will sooner or later be replaced by a more environmentally friendly and economical manufacturing method like the meanwhile well-established lyocell process or the recently developed Ioncell-F process. The development of non-toxic and recyclable cellulose solvents formed the research focus in the last few years.

The improvement of the established technologies will ensure the cost-effective use and the survival of the existing fiber production sites on the fiercely competitive market. The well-engineered technology represents hitherto an advantage over the novel processes. To compete successfully specialty fibers tailored to customer`s requirements have to be developed and established on the market. The understanding of the reactions occurring during the individual process steps will help to prevent undesired yield losses and reduce the formation of degradation products. The application of the results presented in this work should contribute to the improvement of the existing fiber production process.

Further, results useful for development of value-added co-products were obtained in this work. The utilization of co-products will gain in importance in future due to ecological and economic reasons. Therefore further improvements in separation technology and efficiency as well as the investigation of potential applications for hemicellulose are required. Diverse benefits result from the use of hemicellulose as a platform chemical, in particular the availability and the bio-based origin. The conversion of hemicellulose into valuable products meets the demands of the bio-refinery concept at the same time enabling a broad product range.

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