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REVIEW PAPER

Novel concepts of dissolving pulp production

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Abstract Herein, we report about existing and novel dissolving pulp processes providing the basis for an advanced biorefinery. The SO_2–ethanol–water (SEW) process has the potential to replace the acid sulphite process for the production of rayon-grade pulps owing to a higher flexibility in the selection of the raw material source, substantially lower cooking times, and the near absence of sugar degradation products. Special attention is paid to developments that target toward the selective and quantitative fractionation of paper-grade pulps into hemicelluloses and cellulose of highest purity. This target has been accomplished by the IONCELL process where the entire hemicellulose fraction is selectively dissolved in an ionic liquid in which the H-bond basicity and acidity are adequately adjusted by the addition of a co-solvent. At the same time, pure hemicellulose can be recovered by further addition of the co-solvent, which then acts as a non-solvent. The residual pure cellulose fraction may then enter a Lyocell process for the production of regenerated cellulose products.

Keywords Dissolving pulp · Acid sulfite pulp · Prehydrolysis-Kraft pulp · Cold caustic extraction · Ionic liquids · Ioncell process

Introduction

The upturn of dissolving wood pulps (DWP) in the market during the last 10 years may be attributed to a consistent growth of regenerated cellulose fiber production, particularly in China, where 61 % of the current global rayon production capacities are located (Brice 2012). The annual DPW production in 2011 was 4.2 million t, of which 2.9 million t accounted for commodity applications, e.g. rayon, while the residual 1.3 million t were converted to specialties, e.g. to cellulose acetate (Brice 2012).

Market studies clearly indicate that this trend of increasing demand of regenerated cellulose fibers and thus dissolving pulps will prevail during the next decades.

The global production of textile fibers is predicted to increase from 72.5 million t in 2010 to 133.5 million in 2030 by both an increase in per capita consumption (10.5–15.5 kg per capita and year, respectively) and population (6.9–8.3 billion; Haemmerle 2011). The

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inherent physiological properties of cellulose fibers ensure an adequate moisture management that cannot be achieved by synthetic fibers. Since these properties are requested in many fiber products, a minimum constant share of cellulosic fibers, including both natural and man-made fibers, of 33–37 % on the global fiber consumption has been projected (Haemmerle 2011). With this assumption, the annual per capita consumption of cellulosic fibers will increase from its present 3.7–5.4 kg in 2030. At the same time, the cotton production will stagnate at a level of about 26–28 million t per year (3.1 kg per capita in 2030) due to the estimated shrinkage of the cotton growing area and the concomitant increase of the annual specific yield from presently 800 to 925 kg per hectare in 2030. The only way to compensate for the resulting cellulose fiber gap of 1.7 kg per capita is to invest in additional capacities of man-made cellulosic fiber production (viscose, lyocell, cellulose acetate, cupro, etc.), which, in absolute terms, translates into an additional annual global production of 14.8 million t (from the present 4.2 to 19.0 million t in 2030; Shen and Patel 2010). The growing demand for highly purified cellulose pulps is, however, not only limited to textile applications, but it also concerns the manufacture of cellulose acetate for high value-added films, plastics, and coatings as well as cellulose mixed ethers for lacquers and printing, cellulose ethers, and cellulose powder, which have found important applications in the food and pharmaceutical industries. Moreover, dissolving pulps seem to be the preferred substrate for the manufacture of nanofibrillated cellulose (NFC), a future precursor of advanced materials.

Parallel to the necessary investments in new viscose and lyocell fiber capacities, additional capacities in the production of dissolving pulps, the raw material for the manufacture of man-made cellulose fibers, have to be installed. Dissolving pulp refers to pulp of high cellulose content, comprising a minimum amount of inorganic and non-cellulosic organic impurities (Sixta 2006b).

Currently, DWP are produced by the acid sulfite (AS) and the vapor-phase prehydrolysis kraft (PHK) processes, which were both developed in the 1950s. While the former remained technically largely unchanged, a modern displacement cooking procedure was adopted to the steam PHK process (Sixta 2006b). These dissolving pulp technologies, Visbatch® and VisCBC, combine the advantages of displacement technology and steam prehydrolysis (Wizani et al. 1994). They are characterized by their short cover-to-cover times, low energy requirements and very homogeneous and high product quality.

The growing demand for high purity dissolving pulps, however, requires the development of novel process concepts that allow both the realization of advanced biorefinery concepts and the manufacture of pure cellulose pulps, revealing a quality profile comparable to that of cotton linters. Changing from steam to water prehydrolysis (autohydrolysis) allows the selective separation of major parts of hemicelluloses in the form of oligo- and monosaccharides and acetic and formic acids. Unfortunately, sticky precipitates are formed from dissolved acid soluble lignin, which currently hampers the commercial application of autohydrolysis as a pre-treatment of alkaline delignification processes (Leschinsky et al. 2009). Andritz recently developed cooking system upgrades for retrofit to DPW operation in continuous digesters, including a prehydrolysis reactor vessel for water prehydrolysis. In the meantime, this technology has been delivered or is about to be delivered to several customers in Asia (Wiley 2011). For the batch cooking technology, the processability of water prehydrolysis is ensured by an in situ adsorption of the released reactive lignin fractions on activated carbon, as recently suggested (Guetsch et al. 2011; Guetsch and Sixta 2012).

Autohydrolysis of hardwood accelerates the delignification rate during subsequent kraft or soda-anthraquinone (SAQ) pulping, presumably due to better accessibility and the cleavage of LLC bonds as demonstrated by kinetic studies (Schild et al. 1996; Rauhala et al. 2011). Thus, milder cooking conditions, expressed in lower H-factor and/or chemical charges, are sufficient to achieve the requested degree of delignification. However, alkaline delignification methods following autohydrolysis pre-treatment of wood, even under mild conditions, are associated with high cellulose losses due to β-elimination (peeling) reactions. Cellulose yield remains almost unaffected by autohydrolysis up to relatively high intensities, while the degree of polymerization (DP) is decreased by the hydrolytic cleavage of glycosidic bonds, thus creating new reducing end groups (REGs). Since the extent of alkaline peeling reactions is proportional to the concentration of REGs, subsequent alkaline treatment, such as kraft pulping, leads to substantial yield losses (Borrega et al. 2013; Testova et al. 2013). The combination of prehydrolysis with acid sulphite cooking is, however, no alternative because of insufficient delignification owing to the deactivation of lignin structures towards sulfonation (Fasching et al. 2005).

The preservation of cellulose up to very high purities is of utmost importance for the development of a new generation of dissolving pulps. Paper-grade pulps provide a suitable basis for the manufacture of high yield dissolving pulps provided that selective and efficient extraction processes for hemicelluloses can be found. Cold caustic extraction (CCE) is known to selectively extract hemicellulose from pulp (Rydholm 1965). However, so far CCE was only applied subsequent to prehydrolysis-kraft or acid sulfite-hot caustic extraction to achieve very high pulp purity as requested for the production of acetate-grade pulp (Sixta 2006c). Quite recently, researchers directly applied the CCE treatment on a paper-grade pulp for its conversion to a dissolving pulp (Koepcke et al. 2008, 2010a, b; Ibarra et al. 2009, 2010a, b; Sixta and Schild 2009; Schild and Sixta 2010; Wollboldt et al. 2010; Gehmayr et al. 2011). In this way, the cellulose yield of a paper pulp can be fully retained while substantial amounts of short-chain material are removed. This is expressed in a high alkali resistance, e.g. R18 >97.5 %, and a narrow molar mass distribution (MMD), both exceeding the values of a conventional prehydrolysis-kraft pulp. However, the efficiency of hemicellulose removal is quite limited, especially for softwood kraft pulps, since glucomannan is only partially extracted by aqueous sodium hydroxide. The treatment of a pine kraft pulp with a 10 w/w% (111.7 g/L) sodium hydroxide solution at 30 °C for 60 min afforded only 73 % hemicellulose removal (91 % arabinoxylan and 50 % glucomannan), while 85 % of the xylan was extracted from an Eucalyptus kraft pulp when treated with a sodium hydroxide concentration of 8.8 w/w% (100 g/L) at 30 °C for 30 min (Gehmayr et al. 2011; Testova and Sixta 2012). Consequently, the high residual hemicellulose content of CCE-treated paper pulps does not allow their use for the conversion to an acetate-grade pulp (Wilson and Tabke 1974).

Cold alkali treatment of a pulp is associated with a gradual change of the cellulose I crystal structure into Na-cellulose I and, upon regeneration, to cellulose II modification, when the sodium hydroxide concentration exceeds 8 w/w% (Sixta 2006c). The change in the cellulose crystalline lattice which, when subjected to drying, alters the fiber structure and subsequent reactivity. For example, dried mercerized cellulose is resistant to acetylation under the normal processing conditions while it is usually reactive in the viscose process. The reported yield losses are 1.2–1.5 % per 1 % increase in alpha-cellulose content (Rydholm 1965), 1.2–1.8 % for a 1 % gain in R10 (Hinck et al. 1985) and 1.4 % per 1 % decrease in xylan in the case of a CCE treatment on hardwood prehydrolysis-kraft pulps (Sixta 2006c).

Kettenbach and Stein reported that, alternatively to sodium hydroxide, an aqueous solution of 5–7 w/w % nitren, a metal complex of tris-(2-aminoethyl)amine and nickel (II) hydroxide, selectively extracts xylan from a hardwood paper-grade pulp (Kettenbach and Stein 2002). Studies on the optimization of nitren extraction revealed that the maximum xylan removal on a birch kraft pulp was 90 % at a pulp consistency of 6.2 w/w%, a nitren concentration of 6 w/w% at 30 °C and 30 min retention time (Puls et al. 2006). Under these conditions 6 % of the initial cellulose was also dissolved which represents a specific yield loss of about 1.3 % per 1 % decrease in xylan. Thus, the selectivity of a nitren extraction is comparable to that of a CCE treatment, however, at a slightly higher purification efficiency (90 vs. 85 %; Janzon et al. 2006). The fact that the cellulose I structure is fully retained after a nitren extraction at whatever nitren concentration is a further advantage over a CCE treatment (Janzon et al. 2008). The method is suitable for sulfite and kraft pulps, but it is restricted to hardwood because nitren is unable to mobilize residual mannan, presumably due to the cis configuration of β-D-mannose. Nevertheless, the production and recovery of nitren features some difficulties. Many nickel compounds are known as carcinogenic and Ni itself initiates allergic reactions. Washing with lactic acid in two cycles with a total washing time of 60 min was necessary to reach a nickel concentration of 12 ppm in the final eucalypt pulp (Janzon et al. 2006).

In conclusion, novel process concepts need to be developed that allow the selective and quantitative removal of hemicelluloses and lignin to realize advanced biorefinery concepts and to satisfy the growing demand for high purity dissolving pulps. Very recently, we discovered that mixtures of an ionic liquid with a molecular co-solvent are capable of almost quantitatively dissolving hemicelluloses from both hardwood and softwood paper-grade pulps, while cellulose yield remains unaffected (Sixta et al. 2012).

This study provides an overview on commercial and non-commercial process concepts for the manufacture of dissolving pulps comprising both further developments of existing technologies as well as novel approaches.

Materials and methods

Raw materials

Birch, spruce and pine wood chips were delivered from a pulp mill in Finland and *Eucalyptus globulus* from plantations in Uruguay. The chips were screened (SCAN-CM 40:01) upon delivery and subsequently stored in a freezer. The composition of the wood chips is summarized in Table 1 (% on odw).

Commercial ECF-bleached birch and pine kraft pulps comprising an (arabino) xylan content of 25.4 and 8.3 %, a (galacto)glucomannan content of 1.0 and 7.9 % and a cellulose content of 73.6 and 83.8 %, respectively, were used for the conversion to a dissolving pulp by CCE and IONCELL treatments. The polymeric carbohydrate composition of the pulps was calculated from their neutral sugar composition on the basis of Janson's conversion formulae (Janson 1974).

1-Ethyl-3-methylimidazolium acetate ([emim][OAc], 98 %) was purchased from Iolitec GmbH, Germany.

Autohydrolysis

Hot water extractions were conducted in a 10 L batch reactor equipped with a heat exchanger and temperature control. A predetermined amount of deionized water was added to reach a liquid-to-wood (L:W) ratio of 3:1 g/g. A high-pressure pump was used to continuously recirculate the water through the chip bed. The intensity of *standard* autohydrolysis was described by the P-factor using an activation energy of 125.6 kJ/mol as determined for the removal of fast reacting xylan (Sixta 2006a), while for the intensity of *reinforced* autohydrolysis, an activation energy of 180 kJ/mol was applied to compute a modified P-factor, log P-X_S, corresponding to the removal of the recalcitrant xylan fraction in birch wood (Borrega et al. 2011).

Table 1 Composition of wood chips

Species	Cell	(A)X	GGM	KL	ASL
Birch	43.1	27.2	2.5	21.7	4.4
E. globulus (Sixta et al. 2011b)	48.7	21.1	1.9	22.7	4.7
Spruce (Iakovlev and Heiningen 2012)	44.1	8.0	17.7	27.7[a]	
Pine	41.1	8.5	17.2	25.9	0.7

Calculation according to Janson (1974)

KL Klason lignin, *ASL* acid soluble lignin

[a] Total lignin

Pulping experiments

SAQ of birch chips and SEW treatments of spruce chips were conducted in an oil-bath reactor, containing eight rotating autoclaves of 225 mL each. In SAQ cooking, an aqueous solution containing caustic soda (22 % NaOH on odw) and AQ (0.1 or 1.0 % odw) was added, reaching a L:W ratio of 3:1 g/g. 0.5 % of sodium borohydride ($NaBH_4$) was added as a reductive stabilization agent to the SAQ pulping liquor. The temperature in the reactor was raised to 150 °C and kept constant for 60 min, reaching an H-factor of about 200 h. SAQ pulping of *E. globulus* chips was conducted in a 10-L digester with forced liquor circulation, using the continuous batch cooking (CBC) mode (Schild and Sixta 2011). The same equipment was used for AS pulping of spruce chips with the standard procedure being described in (Sixta et al. 2004). The detailed composition of the AS cooking liquor and reaction temperatures is provided in the "Results" part. The cooking liquor for SEW fractionation of spruce chips was prepared by injecting gaseous SO_2 into a cold ethanol/water mixture (55 % v/v) until a concentration of 1.88 mol/L was reached. More detailed information can be found in Iakovlev and Heiningen (2012). Selected SEW and PHSAQ pulps were ECF bleached to full brightness. The applied bleaching sequences are listed in Table 4.

Pre- and post-alkaline extraction

Alkaline pre- and post-extraction (CCE) of *E. globulus* chips and kraft pulp are described in Sixta et al. (2011b) and those of birch chips in Sixta et al. (2011a).

Ioncell process

The paper pulps were treated with a solvent system in a vertical kneader at 60 or 80 °C for 0.5–6 h at consistencies ranging from 3 to 10 w/w%. The solvent system consisted of an [emim][OAc]-water mixture with a water content ranging between 10 and 30 w/w%. A press filter was used to separate the undissolved material at 60 °C (metal fleece with an average pore diameter of 20 µm). The dissolved hemicellulose was precipitated by further addition of water (non-solvent). The solvent mixture was removed by thorough washing in hot water and the washed and dried cellulose and hemicellulose fractions were analyzed.

Analyses

Chemical composition of wood and pulp samples was determined after a two-stage total hydrolysis, according to the analytical method NREL/TP-510-42618. The ASL was measured in a Shimadzu *UV-2550* spectrophotometer at a wavelength of 205 nm and using an absorption coefficient of 110 L/(g cm) (Swan 1965). The monosaccharides were determined by HPAEC-PAD in a Dionex ICS-3000 system. Based on the amount of neutral monosaccharides, the cellulose and the hemicellulose content in wood and pulp samples were determined according to Janson's formulae (Janson 1974). The kappa number and intrinsic viscosity of the pulps were determined according to the SCAN-C 1:100 and SCAN-CM 15:99 methods, respectively. Alkali resistance in 10 wt% (R10) and 18 wt% (R18) NaOH solutions was determined, respectively, according to DIN54355 (1977).

Pulp reactivity was measured following a modified protocol by Treiber et al. (1962) as described by Huepfl and Zauner (1966) for viscose preparation and characterization in terms of filterability and particle content. Particles in a range of 3–155 µm were measured on a Pamas device operating according to the light blockade principle.

MMD of pulps was determined by gel permeation chromatography. About 500 mg of the pulp sample was accurately weighted into a sample bottle. Prior to the analyses, the samples were activated by a water—acetone—*N*,*N*-dimethylacetamide (DMAc) sequence. Approximately 50 mL of MilliQ-water was added to the pulp sample. The samples were kept in water under gentle stirring for more than 6 h. The water activated sample was filtered and rinsed with acetone before it was transferred to a dry bottle where acetone was added and stirred for more than 2 h. After acetone has been removed by filtration, the residue was immersed in 20–40 mL DMAc and kept there for at least 16 h. The activated samples (50 mg each) were dissolved in 90 g/L lithium chloride (LiCl) containing DMAc at room temperature and under gentle stirring. The samples were then diluted to 9 g/L LiCl/DMAc, filtered with 0.2 µm syringe filters, and analyzed in a Dionex Ultimate 3000 system with a guard column, four analytical columns (PLgel Mixed-A, 7.5 × 300 mm) and RI-detection (Shodex RI-101). Flow rate and temperature were 0.75 mL/min and 25 °C, respectively. Narrow pullulan standards (343–2,500 kDa, PSS GmbH) were used to calibrate the system. The molar masses (MM) of the pullulan standards were modified to correspond to those of cellulose ($MM_{cellulose} = q \cdot MM^{p}_{pullulan}$) following recommendation from literature (Berggren et al. 2003). The coefficients $q = 12.19$ and $p = 0.78$ were found by a least-squares method using the data published in their report.

Degree of sulfonation of lignin

Quantitative ^{13}C NMR spectra of Tetraethylammonium-LS ($(CH_3–CH_2)_4N^+$ lignosulfonate$^-$) allow the determination of the DS of the LS following the method of (Li et al. 2008).

Crystallinity

Wide-angle X-ray scattering (WAXS) measurements were carried out under perpendicular transmission geometry with a setup consisting of a Seifert ID 3003 X-ray generator (voltage 36 kV, current 25 mA) equipped with a Cu tube (wavelength 1.54 Å), a Montel multilayer monochromator, and a MAR345 image plate detector. The samples were placed inside metallic sample holder rings 1 mm thick and sealed on both sides with Mylar foil. The calculation of crystal size and crystallinity was carried out as previously presented (Penttilae et al. 2010).

Quantification of cellulose I and cellulose II structure

The generation of the cellulose II structure in the pulp upon CCE was estimated by NMR spectroscopy. Solid state 13C-CP/MAS-NMR investigations were performed with a VARIAN 400 MHz spectrometer with a sample rotation frequency of about 6 kHz, a contact time of 1 ms and a repetition time of 3 s. More informations on the method see elsewhere (Roeder et al. 2006). The ratio of Cellulose I-to-Cellulose II was estimated from the relative height of the C6 resonance at 65.6 ppm.

Kamlet–Taft parameters

The Kamlet–Taft parameters were determined from the absorption peaks of the three dyes, Reichardt's dye (RD, range 518–585 nm), *N*,*N*-diethyl-4-nitro-aniline (DENA, 402–414 nm), and 4-nitroaniline (NA, 406–398 nm). The dyes were weighed as is and mixed with the ILs to a peak absorbance of 0.2–2.5 AU (i.e., concentrations were RD 1.1, DENA 0.24, and NA 0.27 mmol/g). A Varian UV–VIS spectrometer equipped with a thermostat (precision ±0.1 °C) was used. Deionized water was measured for background subtraction. Spectra were collected at a resolution of 1 and 10–30 nm of absorbance data around the peak was fitted with a Gaussian function in order to precisely locate the maxima (ν_{max}). The result was a resolution exceeding that of the instrument (1 nm).

More details on the evaluation of the Kamlet–Taft parameters can be found elsewhere (Doherty et al. 2010; Hauru et al. 2012).

Results and discussion

Acidic fractionation processes

AS pulping offers a good basis for the realization of the biorefinery concept, allowing the recovery of the three lignocellulosic polymers as pure cellulose pulp (DWP), monomeric sugars, and lignosulfonate in economically attractive quantities. In several industrial AS dissolving pulp plants, products from hemicelluloses (furfural, ethanol, yeast, acetic acid) and lignin (lignosulfonates, vanillin) are produced, enhancing the profitability of the mills. AS pulping, however, shows immanent drawbacks characterized by its low flexibility in the selection of raw material sources, long overall cooking time due to very slow impregnation, inefficient recovery of cooking chemicals, and the conversion of substantial amounts of monomeric sugars to aldonic acids. SEW pulping has the potential to be a viable alternative to metal-based acid sulfite cooking (Iakovlev and Heiningen 2012). The presence of ethanol in the cooking liquor moderates its acidity and allows fast transport of the pulping agents to the reaction sites inside the wood. In this way, the overall cooking time can be substantially reduced. Further, ethanol is known to be a better solvent for lignin and lignosulfonate than water. The absence of a base in the process modifies the recovery cycle to simple distillation of ethanol and unreacted SO_2. Ethanol does not participate in the reactions and can thus be recovered almost quantitatively. Although the pK_a of $SO_2 \cdot H_2O$ increases from 1.8 in pure water to 2.7 in 55 v/v% ethanol–water at room temperature, the acidity of the SEW cooking liquor is higher as compared to that of an AS cooking liquor owing to higher initial SO_2 concentration (e.g. 1.88 vs. 1.01 mol/L for SEW and AS cooking liquors, respectively) and the absence of a base, which also accounts for the rather low $[HSO_3^-]$ (Wedzicha and Goddard 1991). Figure 1 reveals a significantly higher viscosity reduction rate of an SEW treatment compared to AS cooking of spruce, which confirms the higher proton activity of the former. SEW treatment causes also a higher delignification rate than MgS pulping (Fig. 2), but, due to the high $[HSO_3^-]$ of the latter, the difference between the rates is much smaller than between those of depolymerization.

The major difference between the two acidic fractionation methods is reflected in the degree of sulfonation (DS) of the dissolved lignin. The lignosulfonates derived from AS cooking exhibited an average DS of 0.50 (Wollboldt 2011), while the one from SEW cooking showed an average DS of only 0.20. A closer look confirms the heterogeneous sulfonation pathway of spruce lignin through SEW cooking, resulting in the formation of two lignin fractions, one very low sulfonated lignin ($S/C_9 = 0.12$), which precipitates upon the evaporation of ethanol, and a second, higher sulfonated, water-soluble lignin ($S/C_9 = 0.29$). The DS values and the mass fractions of the lignosulfonates present in the spent liquors after SEW and MgS fractionation of spruce wood are listed in Table 2.

The low $[HSO_3^-]$ also prevents the formation of aldonic acids from dissolved monosugars by a redox reaction, which allows higher and easier sugar recovery. Further, the presence of ethanol in the cooking

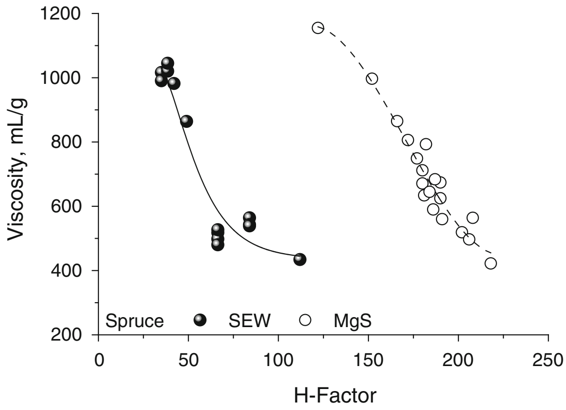

Fig. 1 Intrinsic viscosity as a function of H-factor for SEW and MgS treatment of spruce wood chips. SEW conditions: Initial SO_2 concentration = 1.88 mol/L, ethanol content in cooking liquor = 55 v/v%, L/W ratio = 6:1, temperatures 135 and 150 °C. H-factors 33–112. MgS conditions: Initial SO_2 concentration = 1.01 mol/L, initial MgO concentration = 0.225 mol/L, L/W ratio = 3.2, temperature = 145 °C, H-factors 122–218 (Sixta 2006d)

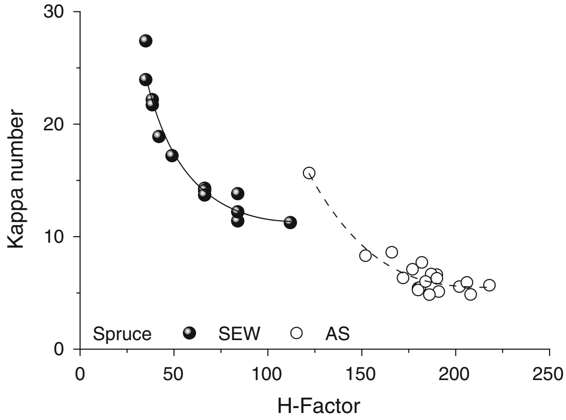

Fig. 2 Kappa number as a function of H-factor for SEW and MgS treatment of spruce wood. SEW and MgS fractionation conditions see Fig. 1

Table 2 Degree of sulfonation of the dissolved lignin derived from spruce SEW and MgS cooking

Lignin fractions	Dissolved lignin fraction	SEW S/C9	MgS S/C9
Soluble	0.43	0.29	
	1.00		0.50
Insoluble	0.57	0.12	
Total	1.00	0.20	0.50

SEW conditions: Initial SO_2 concentration = 1.88 mol/L, ethanol content in cooking liquor = 55 v/v%, L:W = 6:1, temperature 150 °C, H-factor = 66. MgS conditions: Initial SO_2 concentration = 1.01 mol/L, initial MgO concentration = 0.225 mol/L, L/W ratio = 3.2, temperature = 145 °C, H-factor = 180

liquor obviously suppresses yield loss reactions, such as the dehydration of sugars and consecutive reactions thereof, but seemingly also hinders the full hydrolysis of oligosugars to monosugars. Overall, SEW fractionation of spruce wood yields 18.6 % on odw of neutral sugars in the spent liquor which is 59 % higher than present after MgS cooking (Table 3). However, the proportion of monosugars accounts only between 50 and 60 % of the total, while it is close to quantitative (86–95 %) in the case of MgS cooking. The SEW liquor is almost free of furanic compounds (0.04 % on odw) and aldonic acids (0.02 % on odw) which is advantageous for the utilization of sugars both regarding their separation efficiency and the downstream costs. The generation of furfural and/or hydroxymethylfurfural is also relatively low under the selected MgS cooking conditions (0.26 % on odw) and should not have any dramatic impact on the fermentability of the sugars (Sklavounos et al. 2012). However, the formation of aldonic acid during MgS cooking is substantial (3.6 % on odw) due to the high [HSO_3^-], which negatively affects the efficiency of neutral sugar recovery through crystallization, chromatographic separation and membrane filtration (Heikkila et al. 1999).

Delignification to very low kappa numbers as known from AS dissolving pulp cooking is, however, not possible in SEW cooking owing to the generation of less sulfonated and thus soluble lignin fractions (Fig. 2). At a given yield or viscosity level, the kappa number of AS pulps is 6–10 units lower as compared to SEW pulps (Fig. 3). Spruce AS dissolving pulps are known to reach kappa numbers of about 5 after cooking, while SEW dissolving pulps hardly exhibit kappa numbers below 10, even not at lower pulp viscosities. The kappa number almost doubles when the L/W ratio is decreased from 6:1 (13.7) to 3:1 (24.2), presumably due to the limited solubility of the degraded lignin fractions. The higher initial lignin content of the SEW pulps is responsible for the higher OXE (oxidation equivalents) demand to reach the target brightness of 90 % ISO (Table 4). Although SEW cooking of spruce at low L/W ratio shows poor delignification, it revealed higher purification selectivity than SEW cooking at high L/W ratio, as exemplified in Fig. 4 by the relationship between pulp

Table 3 Total sugars dissolved in the spent liquor

Parameter	SEW	MgS
Neutral sugars	**185.6**	**117.1**
Glucose	22.6	22.9
Mannose	88.2	66.0
Galactose	24.3	6.9
Xylose	40.5	19.6
Arabinose	10.0	1.7
Furans	**0.4**	**2.6**
Furfural	0.3	1.9
HMF	0.1	0.7
Aldonic acids	**0.19**	**35.6**
Xylonic acid	0.11	18.0
Mannonic acid	0.08	17.6

Bold values denote the sums of the different classses of compounds originating from sugars

SEW conditions: Initial SO_2 concentration = 1.88 mol/L, ethanol content in cooking liquor = 55 v/v%, L/W = 6:1, temperature 135 °C, H-factor = 42. Pulp yield (screened) = 47.9, Kappa number = 9.1 (Iakovlev and Heiningen 2012). MgS conditions: Initial SO_2 concentration = 1.07 mol/L, initial MgO concentration = 0.24 mol/L, L/W = 3.2, temperature = 145 °C, H-factor = 180. Pulp yield (screened) = 45.5 %, Kappa number = 4.9. Values are given as anhydrosugars in kg/t of oven dry wood (odw) (Sixta 2006d)

viscosity and the amount of residual hemicelluloses. At this point, the reason for this behavior is not fully understood. It may be hypothesized that with decreasing L/W ratios, the difference in the proton concentration in the two phases is minimized by the increasing concentration of the released lignosulfonate anions entrapped inside the pulp. In other words, the accumulation of the electrolyte should result in an increase in the concentration of H_3O^+ ions in the pulp phase following Donnan's theory of membrane equilibrium (Zaranyika and Madimu 1989). The higher reactivity of hemicelluloses compared to cellulose towards acid catalyzed hydrolytic chain cleavage explains the higher purification selectivity of SEW fractionation at low L/W ratio (Fig. 4). In this way it was possible to achieve acceptable rayon pulp properties without hot caustic extraction, as exemplified for the SEW-2 pulp (Table 4). Overall, ECF-bleached SEW and AS dissolving pulps exhibit comparable properties. They both meet the specification requested for rayon pulps (Table 4). This was confirmed by a good to very good quality of the viscose prepared by the SEW-2 pulp using Treiber's method (Treiber et al. 1962; Fig. 5).

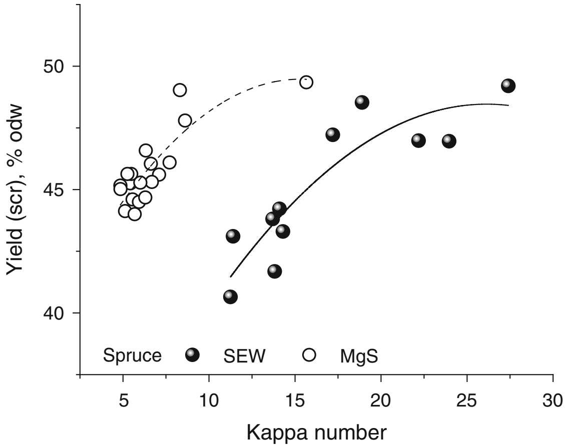

Fig. 3 Yield versus kappa number of spruce AS and SEW cooks. SEW and MgS fractionation conditions see Fig. 1

Alkaline fractionation processes

The manufacture of high-purity dissolving pulps (R18 >96 %) with a narrow MMD is conveniently accomplished by the two-stage PH-K or PH-SAQ processes. Currently, the sugars and acetic acid from the hydrolysate are not recovered prior to the alkaline delignification step because prehydrolysis is almost exclusively conducted in vapor-phase. Now, with the development of technically feasible water prehydrolysis processes for the continuous and batch production, the hydrolysate can be used as a source for food additives and platform chemicals (Wiley 2011; Guetsch and Sixta 2012). The concomitant production of platform chemicals and rayon pulp from birch wood was studied in lab trials using both silver birch (*Betula pendula*) and *E. globulus*. While the amounts of xylose, xylo-oligosaccharides, and acetic acid in the hydrolysate were confirmed experimentally, the final yields of the purified platform chemicals, furfural and acetic acid, were assumed, based on literature data and industrial experience. The potential of increasing the pulp yield through the addition of sodium borohydride ($NaBH_4$) to the cooking liquor was studied in the case of birch wood. As shown in Table 5, the addition of $NaBH_4$ resulted in 1.5 % higher cellulose and also 0.6 % higher xylan yield. Thus, the addition of REG stabilizers is no viable option, because xylan is preferentially preserved which, in the end, deteriorates cellulose purity. Attempts to compensate for the loss in purity by enhanced prehydrolysis intensity resulted in a xylan/yield relationship comparable to that

Table 4 Specification of ECF-bleached SEW- and MgS rayon pulps from spruce (average of two bleaching series)

Process	Sequence	Total yield % odw	OXE t^{-1} pulp	Brightness % ISO	Viscosity (mL/g)	R18 (%)	Xylan (%)	Mannan (%)
SEW-1	EO-D-Q-P	39.8	628	90.2	478	94.4	1.7	1.5
SEW-2	O-D-EP-Q-P	41.7	1,239	89.3	478	93.2	1.7	2.2
MgS	E-O-D-P	40.7	345	89.9	552	94.8	1.7	1.9

SEW-1: 1.88 mol/L SO_2, L/W = 6/1, 60 min at 150 °C, 55 % v/v EtOH, H-factor = 71, kappa number = 13.7; SEW-2: like SEW-1, but L/W = 3/1, H-factor = 60, kappa number = 24.2. MgS: 1.07 mol/L total SO_2, 0.24 mol/L MgO, L/W = 3.2/1, 145 °C, H-factor = 180, kappa number = 4.9

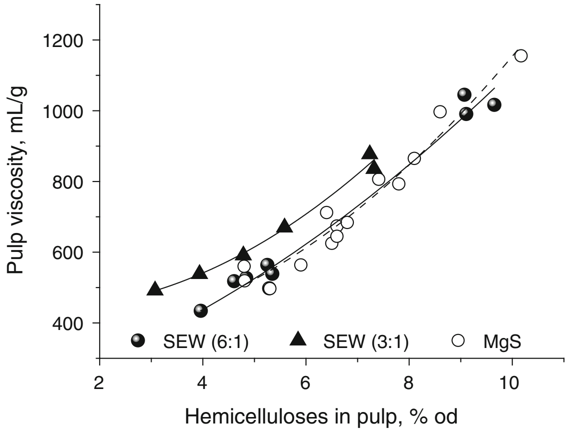

Fig. 4 Pulp viscosities versus hemicellulose contents of unbleached spruce SEW and AS pulps. SEW and MgS fractionation conditions see Fig. 1. The amount of hemicelluloses represents the sum of the neutral xylan and mannan contents in the pulps

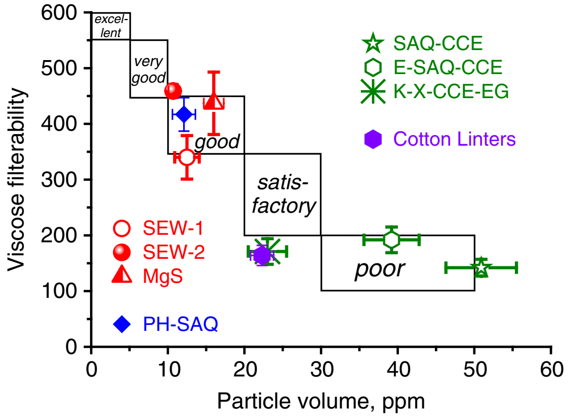

Fig. 5 Filterability versus particle volume of viscose samples prepared from different dissolving pulps: (E)SAQ-CCE (Schild and Sixta 2011), K-X-CCE-EG (Gehmayr et al. 2011), PH-SAQ

without the addition of REG stabilizers (Borrega et al. 2013). Water prehydrolysis allows the recovery of sugars and carboxylic acids, which can be further converted to value-added building block chemicals. From birch (*B. pendula*) prehydrolysis at a L/W ratio of 4.0:1.0 (3.5:1), 65 % (63.5 %) of the total hydrolysate was recoverable. It contained 8.4 % (6.3 %) on odw of xylan of which 50 % (18 %) was of monomeric xylose. The higher proportion of monomeric xylose in the birch hydrolysate can be explained by the higher P-factor that is applied in the prehydrolysis of birch (1000) compared to *E. globulus* (600), to achieve the specification required for a rayon pulp.

The recovery of xylose from the released hydrolysate and its potential conversion to 4.9 % (3.7 %) furfural on odw may significantly contribute to the economy of the fractionation process (see Tables 5, 6). Hence the sales of the DPW production increase by almost 45–60€/t of wood, assuming the current furfural market price of 1,200€/t (~13–18 % of the DPW sales assuming a sales price of 1,000€ per odt dissolving pulp). Despite the high prehydrolysis intensity, the birch PH-SAQ dissolving pulp shows rather low cellulose purity (Table 5), which, however, seems sufficient for rayon application as confirmed by a reasonably good viscose quality (Fig. 5). The use of a wood species of low hemicellulose content, such as *E. globulus*, allows, however, the production of a dissolving pulp with a significantly lower xylan content, while higher yield, as compared to the use of birch wood.

This is particularly important for the production of acetate grade pulp where the minimum requirement on pulp purity is a residual xylan content of 1.2–1.5 %.

In a series of experiments with birch wood, in which the intensity of prehydrolysis was gradually brought to very high levels, the relationship between pulp yield after subsequent SAQ cooking and the associated xylan content and the viscosity of the unbleached pulps was examined.

Table 5 Summary of process conditions, product specification and yields of alkaline fractionation of birch wood

Processes	Kappa	Unbleached		ECF bleached pulp					Extract		By-products	
		Xn (%odw)	Yield (%odw)	Yield (%odw)	R18 (%)	Xn (%)	[η] (mL/g)	B (%ISO)	Xyl (%odw)	AcOH (%odw)	F (%odw)	AcOH (%odw)
PH-SAQ	8.3	5.0	36.8	34.1	95.8	4.9	507	90.4	8.4[a]	1.2	4.9	1.0
PH-SAQ-B	8.2	6.3	38.3	36.2	95.5	5.9	572	91.4	8.4[a]	1.2	4.9	1.0
K-CCE100	19.2	24.3	51.5	40.8	98.2	7.1	n.d.	n.d.	7.7[b]	n.d.		

PH-SAQ(B), PH: L/W = 4/1; P-factor = 1,000; 65 % of hydrolysate recovered

[a] 50 % monomer, 50 % oligomer. SAQ(B): L/W = 3.5/1; 22 % NaOH on odw; 0.1 %AQ; (0.5 % SBH); H-factor = 300–350; O-A-D-EP-P sequence

K-CCE100, K: L/W = 3.5; EA = 22 % odw, 35 % sulfidity; 160 °C; H-factor = 800. CCE (Alekhina et al. 2013): 5 % consistency, 100 g NaOH/L, 23 °C, 60 min; O-CCE-D-EOP-P sequence

[b] Xylan yield = 80 % of the amount in the UF-retentate by sulfuric acid precipitation, purification, drying

By-products, Furfural yield (80 mol %) according to (Xing et al. 2011); AcOH yield (80 w %) based on industrial experience (Sixta 1986)

Table 6 Summary of process conditions, product specification and yields of alkaline fractionation of *E. globulus* wood

Processes	Kappa	Unbleached		TCF bleached pulp					Extract		By-products	
		Xn (%odw)	Yield (%odw)	Yield (%odw)	R18 (%)	Xn (%)	[η] (mL/g)	B (%ISD)	Xyl (%odw)	AcOH (%odw)	F (%odw)	AcOH (%odw)
PH-K	6.5	3.3	38.0	37.0	96.6	2.7	440	90.9	6.3[a]	1.3	3.7	1.0
K-CCE80	13.1	19.5	52.9	42.6	97.4	4.8	n.d.	n.d.	6.6	n.d.		
K-CCE100	13.1	19.5	52.9	41.8	98.1	3.8	n.d.	n.d.	7.0[a]	n.d.		
K-CCE120	13.1	19.5	52.9	41.8	98.3	4.5	n.d.	n.d.	6.7[b]	n.d.		

PH-K, PH: L/W = 3.5/1; P-factor = 600; 63.5 % of hydrolysate recovered

[a] 18 % monomer, 82 % oligomer. K = CBC cook: 12 % EA on odw for neutralization; 30 g/L NaOH in cooking liquor; 60 % sulfidity; 160 °C; H-factor = 300. O-Z-P sequence (Schild and Sixta 2011)

K-CCE, K = CBC cook: 25 g/L NaOH in cooking liquor; 70 % sulfidity; 160 °C, H-factor = 600. CCE: 10 % consistency, 80/100/120 g/l NaOH, 30 °C; 30 min; O-CCE-Z-P sequence

[b] Xylan yield = 80 % of the amount in the UF-retentate by sulfuric acid precipitation, purification, drying

By-products, Furfural yield (80 mol %) according to (Xing et al. 2011); AcOH yield (80 w %) based on industrial experience (Sixta 1986)

Figure 6a reveals the substantial yield loss from 34 to 23 % on odw when the xylan content is reduced from 4.5 to 1.5 % by intensified prehydrolysis.

The low pulp yield combined with the low pulp viscosity of 300 mL/g excludes this production concept for the manufacture of acetate grade pulps. Hardwoods with substantially lower xylan content than birch, such as different Eucalyptus species, e.g. *E. globulus*, *urograndis* or *saligna*, might be a suitable raw material source for the production of low-quality acetate grade pulp by means of PH-K or PH-SAQ cooking only, thus avoiding additional refining steps (Sixta 2006a).

In recent years, several studies focused on the conversion of paper-grade to dissolving pulps by simply extracting the hemicelluloses (mainly xylan also in the case of SW pulp) in aqueous 1.5–3.0 M NaOH solution at 20–35 °C (CCE; Gehmayr et al. 2011; Schild and Sixta 2011). In this way, cellulose yield is not affected, which constitutes a clear commercial benefit over the PH-K procedure. Further, the CCE-treated kraft pulps (K-CCE) reveal a higher alkali resistance, expressed as R18, and a more narrow MMD than the PH-K-pulps (Schild and Sixta 2011).

However, an alkali-insoluble xylan fraction of high molar mass remains in the pulp even at high NaOH

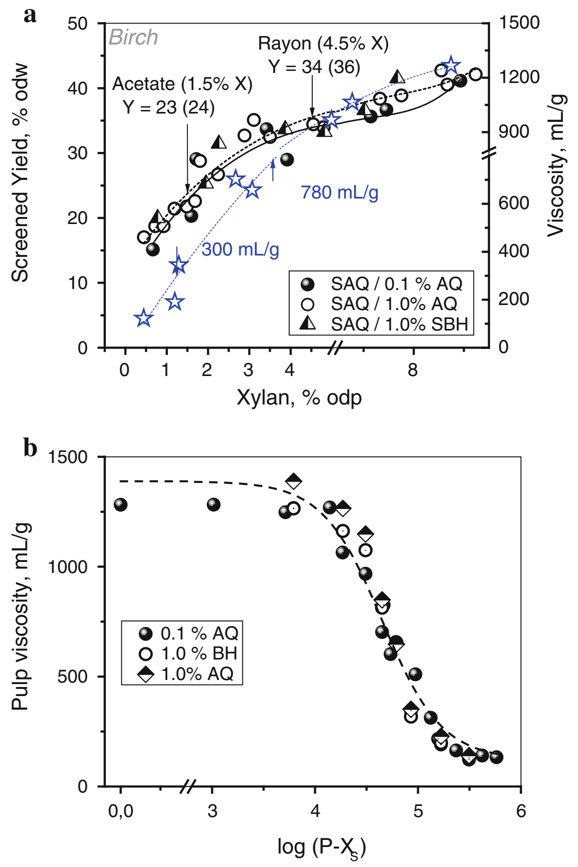

Fig. 6 **a** Yield and viscosity related to the xylan content in a PHSAQ pulp as a function of prehydrolysis intensity expressed as log(P-X_S) as shown in **b** (Borrega et al. 2013)

concentration (Wollboldt et al. 2010). The amount of this alkali-resistant xylan again depends on the wood source and the alkali concentration as demonstrated in Tables 5 and 6. Further drawbacks of a CCE treatment constitute the partial conversion to cellulose II occurring at NaOH concentration >2 M, as revealed in Fig. 7, as well as the aggregation of the microfibrils, which, upon drying, results in a compaction of the supramolecular structure. These alterations of the cellulose structure, possibly together with the entrapped high molar mass xylan, partly explain the poor quality of the viscose made from CCE-treated pulps (Fig. 5). Different to PH-K and AS dissolving pulps, the outer cell wall layers, P and S1, of CCE-treated paper-grade pulps are preserved to a greater extent (Sixta 2000; Schild and Sixta 2011). Thus, the swelling capacity of the S2 is restricted by the rigidity of the outer cell wall layers. The reduced swelling capability in turn causes a lower accessibility and, therefore, lower filter values with high particle numbers, as illustrated in Fig. 5. The high swelling resistance due to a thick primary wall (Temming and Grunert 1973) is presumably also the reason for the poor viscose quality prepared from cotton linters (Fig. 5). It was shown that an endoglucanase post-treatment could improve the accessibility of a CCE-treated kraft pulp, which translates to a slight improvement of the viscose pulp reactivity (Fig. 5). At the same time, it allows the precise adjustment of the DP of the pulp (Gehmayr et al. 2011).

The undiluted filtrate of the CCE stage is a rewarding source of polymeric xylan because the amount of concomitant impurities, such as lignin, extractives or hydroxyacids, alkaline sugar degradation products, is low. In a first step, the xylan is concentrated by ultrafiltration followed by diafiltration to maximize the xylan-to-NaOH ratio. The xylan is precipitated by the addition of an anti-solvent, such as ethanol or isopropanol, or simply by acidification with a strong mineral acid. The xylan yield depends mainly on the raw material source and the conditions in the CCE step. From a birch kraft pulp, 7.7 % of xylan on odw and from a *E. globulus* kraft pulp, 6.6 % (Sixta and Schild 2009) to 7.0 % (Table 6) of xylan on odw were isolated as dry powder when using 2.5 M NaOH solution at 20 °C (Alekhina et al. 2013) and 2.25–3.0 M NaOH solution at 30 °C, respectively (Tables 5, 6). Since polymeric xylan from alkali extraction of hardwood has no definite market yet, no value can be attributed to this product. For example, alkali-extracted xylan can be modified to a film for packaging application after derivatization to a water soluble polymer as recently demonstrated by the conversion to carboxymethyl xylan of different DS values (Alekhina et al. 2013). It also can be transferred to a paper pulp production line where it contributes to a higher yield and better tensile stiffness properties (Vaaler 2008).

Ioncell process

Although about 50 % of the hemicelluloses and about 10 % of cellulose are lost during kraft cooking (Sjoestroem 1993), it is by far the most selective commercial process for the separation of lignin from lignocellulosic biomass. Thus, the resulting paper-grade pulp is the most attractive raw material for the

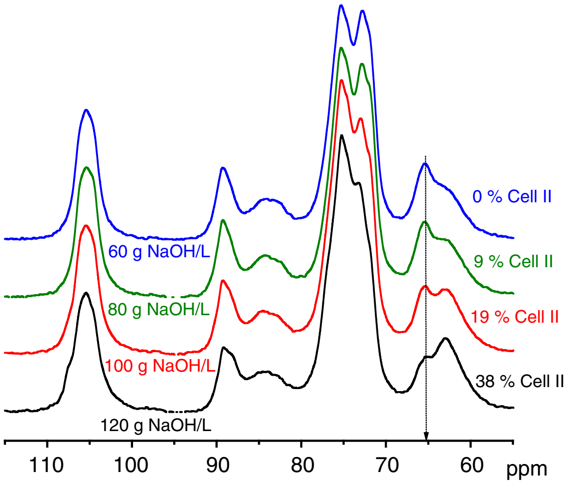

Fig. 7 ^{13}C-CP/MAS spectra of CCE-treated *Eucalyptus globulus* Kraft pulps (K-CCE): Effect of the NaOH concentration during the CCE treatment on the generation of cellulose II structure

manufacture of pure and high molar mass cellulose and hemicelluloses, provided that a process can be developed that allows the selective separation of these polymers. As previously shown, the existing protocols for the removal of hemicelluloses, such as autohydrolysis or alkaline extraction, are all accompanied by unwanted side and degradation reactions or partial conversion of cellulose I to cellulose II. This can largely be avoided by solvent extraction using an aqueous Ni(tren) solution (Puls et al. 2006; Janzon et al. 2008). However, this protocol is handicapped by the necessity of an effective removal of the residual nickel and by the fact that glucomannan from softwood pulp remains almost insoluble under these extraction conditions.

In 2002, Rogers et al. first demonstrated that some ionic liquids (ILs) could solubilize cellulose (Swatlowski et al. 2002). Currently, [emim][OAc] is regarded as one of the best, if not the best cellulose solvent. In an attempt to predict the cellulose dissolution properties of ILs, the empirical concept of net-basicity, β-α, was suggested, which accounts for the acidity imparted by the cation (Hauru et al. 2012). It was shown that all ILs reported to dissolve cellulose are located in an empirical solubility window defined by $0.35 < \beta\text{-}\alpha < 0.9$ with $\beta > 0.85$, expressing a necessary balance between acidity and basicity.

In the considerations to find a solvent system that could selectively dissolve hemicelluloses from a hemicellulose-rich pulp, e.g. paper-grade kraft pulp, it was hypothesized that the requirements for a solvent regarding H-bond basicity are lower as compared to those for cellulose-dissolving ILs. The lower molar mass, the amorphous structure, and the reduced ability to form inter- and intramolecular H-bonds due to the absence of the exocyclic hydroxymethyl group should facilitate dissolution. Indeed, the addition of a defined amount of a molecular co-solvent, e.g. water, to [emim][OAc] to lower H-bond basicity, β, and the net basicity, β-α, was successful in the quantitative and selective dissolution of hemicelluloses from a hemi-rich paper-grade pulp (Fig. 8), while both polymers remained completely unchanged in molar mass and yield (Fig. 9).

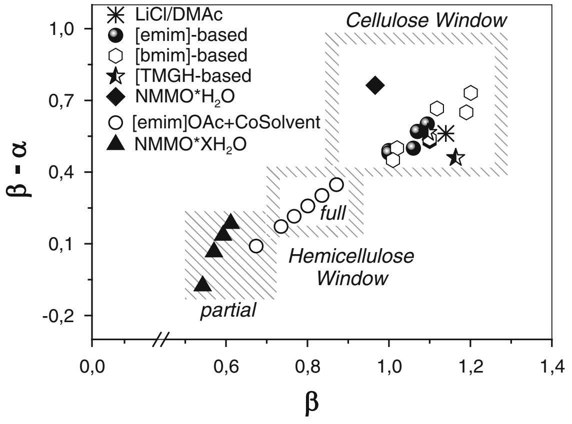

Fig. 8 Net basicity, β-α, plotted against β, showing the solubility windows for cellulose and hemicellulose, respectively

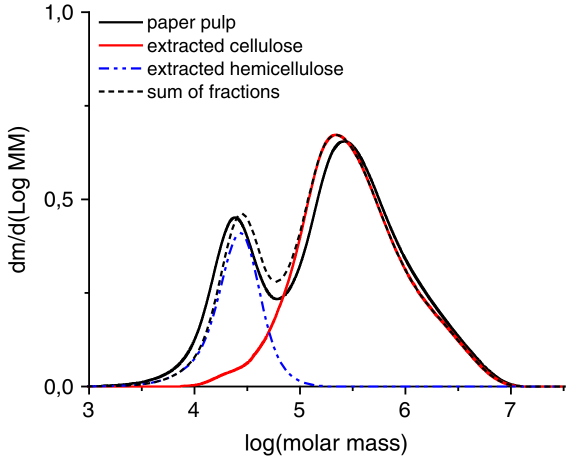

Fig. 9 Molar mass distribution of birch kraft pulp and the pure components, cellulose and xylan, separated thereof by selective dissolution of the latter in [emim]OAc + Co-solvent

In this way, a new process, IONCELL, was developed, which allows the conversion of paper-grade pulp from either softwood or hardwood to a dissolving pulp of highest purity comprising a hemicellulose content lower than 2 % (Froschauer et al. 2013). At the same time, pure xylan can be recovered by further addition of the co-solvent, which then acts as an anti-solvent. The residual pure cellulose fraction may be dissolved in the ionic liquid after having removed the co-solvent to enter a Lyocell process for the production of regenerated cellulose products.

Conclusions

There is no doubt that the existing dissolving pulp processes, AS and P-HK, constitute a commercially attractive biorefinery platform. While biorefinery concepts have already been realized in industrial scale on the basis of the AS process, this was not the case for the PH-K process so far. Now, with the development of technically feasible water prehydrolysis processes, the way is open to utilize the wood hydrolysate as a source for high value-added chemicals. The novel SEW fractionation process has the potential to replace the AS process owing to a higher flexibility in the selection of the raw material source, substantially lower cooking times, and the near absence of sugar degradation products. However, no differences are seen in the properties of the dissolving pulps resulting from both acidic processes.

The general drawback of the industrial processes is that they experience severe cellulose losses once the demand on purity increases beyond the typical rayon grade quality. All existing protocols for the removal of hemicelluloses are associated with loss reactions or, in the case of the conversion of a paper-grade pulp by CCE, with a partial conversion of cellulose I to cellulose II as well as residual hemicelluloses contents too high for the manufacture of high-purity cellulose products.

Based on systematic investigations of the solubility properties of ILs towards polysaccharides, the IONCELL process was recently developed, which permits the production of high-purity dissolving pulps from a hemicellulose-rich paper-grade pulp. Owing to the high selectivity and efficiency, the IONCELL process could be the breakthrough for a new generation of dissolving pulp processes, provided that the selected ILs can be recycled in an economically feasible way.

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