CELLULOSE CHEMISTRY AND TECHNOLOGY

MULTIFUNCTIONAL ALKALINE PULPING, DELIGNIFICATION AND HEMICELLULOSE EXTRACTION

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In this study, multifunctional alkaline pulping was suggested to produce different pulp grades at one mill site, ranging from high-yield paper pulp to high-purity dissolving pulp. In all process modifications, sulfur was successfully replaced by anthraquinone. Autohydrolysis and alkaline pre-extraction were applied to *Eucalyptus globulus* wood chips, followed by kraft and soda-AQ pulping. Alkaline pre-extraction prior to soda-AQ pulping largely preserved the pulp yield, while a substantial amount of xylan could be extracted in polymeric form during the pre-treatment. The resulting pulp revealed characteristics indicating an alternate use – as paper pulp and as dissolving pulp – after further purification with cold caustic extraction (CCE).

The removal of hemicelluloses from kraft or soda-AQ paper pulps by a CCE post-treatment allowed the production of high yield dissolving pulps. The hemi-rich CCE-lye was recycled to soda-AQ pulping, contributing to yield increase by xylan re-precipitation. Alternatively, the CCE-lye could be purified efficiently by ultrafiltration, by concentrating the rather pure and high molecular weight xylan in the retentate for further use.

The results indicated that biorefinery concepts can be realized for alkaline pulping by adopting the proposed modification of multifunctional alkaline pulping.

Keywords: multifunctional alkaline pulping, soda-AQ, kraft, CCE, xylan

INTRODUCTION

For economical and environmental reasons, it is essential that pulping processes assure an appropriate use of all wood components. Therefore, research should be aimed at developing chemical processes which separate wood components as exactly as possible and make them available for value-added further processing or end uses – the concept of biorefinery. The main cooking techniques are the sulfite and kraft or sulphate processes. Both are well-established technologies. At a global scale, kraft pulping accounts[1] for about 89% of the production of chemical pulps, whereas sulphite pulping accounts for about 5%. The situation is completely different in the production of dissolving pulp. The sulfite process is still the dominant technology, with more than 60% market volume. Hemicelluloses and lignin are removed in the same process step. Therefore, the separation of both wood components is difficult and the use as platform chemicals is only possible to a minor degree. Nevertheless, the concept of biorefinery has been realized in several sulfite mills.

The prehydrolysis kraft process becomes more and more important, as due to its well-known benefits, *e.g.* higher pulp qualities and higher cooking capacity. Furthermore, alkaline processes provide the option to extract hemicelluloses before or after pulping in a separate process step, which makes the isolation of the different wood components easier. Much effort has been undertaken to investigate the possibility of hemicellulose removal before alkaline cooking. Van Heiningen and co-workers[2-6] suggest the integration of water prehydrolysis into alkaline pulping concepts to realize a biorefinery. 70% of the hemicelluloses of Southern mixed hardwood could be dissolved as xylo-oligosaccharides during an autohydrolysis step. Extended delignification or cellulose degradation was not observed. At the same time, the content of uronic acid groups in the residual xylan decreased with increasing the extraction time. Delignification during subsequent kraft cooking was accelerated by water pre-extraction, while the yield decreased by 3 to 6% for loblolly pine. At present, water prehydrolysis kraft pulping is not commercially utilized, because of the high investment and energy costs of a water prehydrolysis step. Above all, the waste disposal of the prehydrolysate is even more expensive.[7-9] The formation of sticky precipitates in the prehydrolysate cannot be avoided during the production of dissolving pulps. They are caused by the reactions of dissolved lignin in acid aqueous medium at elevated temperatures. A reduction can be achieved by lower temperatures, which requires prolonged prehydrolysis time or the addition of acid catalysts. However, both approaches have significant disadvantages at an industrial scale and do not fully eliminate precipitation. The current practice of steam prehydrolysis, followed by a neutralization step, avoids this problem. The state-of-the-art of dissolving pulp technologies, Visbatch® and VisCBC, combine the advantages of displacement technology and steam prehydrolysis.[10] They are characterized by short cover-to-cover times, low energy requirements and very homogeneous and high product quality. Nevertheless, these technologies prevent the recovery of valuable carbohydrate degradation products.

Other methods for the extraction of hemicelluloses prior to pulping include near-neutral aqueous pre-extractions at elevated temperatures[11-13] and alkaline pre-extraction at moderate temperatures.[14,15] Generally, the amount of xylan dissolved during autohydrolysis exceeds the amount of hemicelluloses that can be removed during alkaline or near-neutral pre-extraction. Near-neutral and alkaline pre-extraction are only suitable for hardwood, as xylan, the main hemicellulose in hardwood, is dissolved in oligomeric form and can be gained from the process lye, while the softwood galacto-glucomannan is rapidly degraded by the peeling reaction during a hot alkaline treatment and, therefore, it is lost for further valuable usage. After near-neutral extraction with 3% green liquor, the H-factor used in the pretreatment could be saved during pulping, to reach the same extent of delignification as in conventional kraft cooking.[13] The pulp yield after cooking remained the same as for kraft cooking without pre-extraction. The paper making properties of the pre-extracted kraft pulp were as good as or slightly better than those of the control pulp. Wafa Al-Dajani and co-workers[14] used higher NaOH-concentrations at moderate temperatures for alkaline pre-extraction of aspen wood. Hemicelluloses could be removed prior to pulping in a reasonable amount of 40 to 50 kg per tonne of wood chips, while the pulp yield was almost unaffected. Additionally, the sulfur charge could be lowered by up to 20% during subsequent kraft cooking. A comparison of autohydrolysis and alkaline pre-extraction before kraft and soda-AQ-pulping of eucalypt wood confirmed that the alkaline pre-extraction caused acceleration of delignification, which led to a saving of pulping chemicals for both alkaline cooking processes.[15] Simultaneously, a lower formation of hexenuronic acid groups in the pulp gave rise to higher brightness and lower yellowing after bleaching.

Quite recently, the multifunctional alkaline cooking process was suggested, which allows the production of a broad range of pulp grades and the recovery of sugar-based products, following the principle of resource efficiency.[16,17] This concept provides the basis for the production of a new low cost technology for the manufacture of dissolving pulps of all possible grades, ranging from low to very high alpha pulps, parallel to the production of a high-yield paper grade pulp. The concept of multifunctional alkaline cooking allows the removal of short-chain carbohydrates by either autohydrolysis or alkaline pre-extraction. Alternatively, high molecular weight hemicelluloses may be isolated by cold caustic extraction (CCE). The CCE-lye can be utilized either as a pure carbohydrate source for the conversion to building block chemicals or as an additive for paper pulp production, to improve yield and fibre-fibre bonding capability.

EXPERIMENTAL

Wood chips

Eucalyptus globulus wood chips from plantations in Uruguay, supplied by ENCE, were used in all pulping experiments. A fraction >7 mm was used after a laboratory screening, according to the standard method SCAN CM 40:94. The average characteristics of the screened wood chips are given in Table 1.

Cooking experiments

Pilot plant trials were carried out in a 10 L digester with forced liquor circulation, according to the general continuous batch cooking (CBC) concept.[19] All process-related liquors, such as the impregnation and cooking liquors, were already prepared in the tank farm using different tank-to-tank circulation loops. Altogether, seven different cooking concepts were investigated (Table 2).

The effective alkali concentration (EA) in the cooking liquor was kept constant at about 30 g/L for all cookings, except for K, where two series with 30 and 20 g/L were conducted, as well as for SAQH pulping, where EA was reduced stepwise to 10 g/L, to study the effect on xylan reprecipitation. The EA value of the impregnation liquor for K, SAQ and SAQH pulping was kept constant at 15 g/L. Likewise, the P-factor of 600 for PH-K and PH-SAQ cookings, as well as the cooking temperature (160 ºC) for all cookings were kept constant. For SAQ cooking, dispersible anthraquinone Baycel AQ from Kemira Chemie (AQ) in a concentration of 0.5 g/L was added to the white liquor and to the cooking liquor, corresponding to a dosage of 0.15% on wood. Alkaline pre-extraction was carried out for 1 h at 90 ºC with pure white liquor containing an EA of 2.5 mol/L

Table 1
Characteristics of wood chips from *Eucalyptus globulus* from Uruguay

Klason lignin, %	22.7
Acid soluble lignin, %	4.7
Cellulose, %	42.4
Galactoglucomannan (GGM), %	2.2
Xylan,* %	17.0
Arabinan, %	0.4
Rhamnan, %	0.1
Total uronic acids,** %	4.8
Acetone extractives, %	0.6
Ash, %	0.4
Moisture content, %	31.6

* The xylan content was corrected assuming that 60% of the linkages between 4-*O*-methylglucuronic acid (MGA) and the xylan backbone survive the primary and secondary hydrolysis step[18]

** Total uronic acids were calculated from 2.4% MGA, 1.9% galacturonic acid and 0.5% glucuronic acid

Table 2
Abbreviations for the investigated cooking concepts

K	kraft cooking
SAQ	soda-AQ cooking
E-SAQ	alkaline pre-extraction followed by soda-AQ cooking
SAQH	soda-AQ cooking with xylan-enriched lye originating from CCE treatment
PH-K	prehydrolysis kraft pulping
PH-SAQ	prehydrolysis soda-AQ pulping
MgS	magnesium-bisulfite pulping as a reference

SAQH was started with pure CCE-lye as an alkali source. In a subsequent step, the displaced cooking liquor from the previous cooking was utilized as cooking liquor for the following cooking. The target EA concentration was adjusted by means of CCE-lye. For MgS cooking, an H-factor of 75 at the temperature of 145 °C was used, with a total SO_2 of 200 g/kg oven dry wood (odw) to produce a dissolving grade pulp.

Oxygen bleaching and cold caustic extraction

All pulps were subjected to a standard oxygen bleaching stage (O). Oxygen delignification was conducted at 90 °C for 60 min at 12% consistency, on adding 20 kg/t oven dry pulp (odp) of NaOH. The paper grade pulps SAQ, K and E-SAQ with a kappa number ranging from 14.6 to 16.1 were also treated with a CCE after O, for conversion to dissolving pulps. In the CCE-stage, 90 g/L of NaOH were applied at 30 °C for 30 min, at 10% consistency.

Methods

Carbohydrate analysis

The neutral sugar monomers were determined by anion exchange chromatography (AEC) with pulsed amperometric (PAD) detection after a total hydrolysis with H_2SO_4, according to Sixta *et al.*,[20] while the uronic acids were quantified by methanolysis.[21]

Conventional pulp analysis

The well-washed pulps were screened using a flat screen with 0.15 mm slots. All analyses were performed according to Tappi-, ISO- and SCAN standards. Enzymatic peeling of the unbleached pulps was conducted by the method described by Sjöberg *et al.*, combined with the above-mentioned carbohydrate analysis.[22]

Membrane filtration

The laboratory-scale filtration equipment Memcell from KCS Osmota, equipped with a plunger pump, was used for the ultrafiltration of the CCE-lye. The ultrafiltration membrane UP010 from Microdyn-Nadir was applied in the flat-sheet crossflow cell. The molecular weight cut-off of this alkali stable polyethersulfone membrane (MWCO) was of 10 kDa. Temperature was kept constant at 40 °C. The pressure before the membrane was of 250 kPa. The applied flow rate was of 3 L/min.

Two process modes were applied. The permeate was either collected in a separate container during the concentration mode, or led back into the feed reservoir in the closed circuit mode, whereas the retentate was always recycled back to the feed vessel.

RESULTS AND DISCUSSION

Kraft and soda-AQ cooking represented the core process step within the multifunctional alkaline cooking process. The selective removal of hemicelluloses may be achieved by two alternative options: pre-treatments or post-treatments. The pre-treatments involved autohydrolysis (PH) and alkaline pre-extraction (E), while the post-extraction step was represented by cold caustic extraction (CCE). Contrary to mere alkaline cooking, the chemical structure of the removed short-chain carbohydrates was largely preserved. Hemicelluloses showed a polymeric form in the E-extract and CCE-lye, and an oligomeric and monomeric form in the autohydrolysate. Recycling of the CCE-lye containing high molecular weight hemicelluloses to paper pulp cooking allowed xylan enrichment of the paper pulps, as will be demonstrated later.

Cooking performance

The reduction of sulfur was one of our focuses for prehydrolysis pulping as well as for modified cooking with alternative pre- and post-treatments. Therefore, sulfur was replaced by anthraquinone (AQ), stress being laid on the comparative evaluation of the K and SAQ cooking performance, both based on a CBC process technology. The results of the H-factor series were discussed in more detail recently.[23]

The delignification rate in SAQ pulping was slightly lower than in K pulping (Fig. 1), which confirmed the results of other authors on other hardwood species.[24] Vitta,[25] on the contrary, reported a higher delignification rate in SAQ pulping, compared to K pulping, using sweet gum. The reason for this discrepancy might be the variation in the lignin structure among different hardwood species and the different effective concentrations of AQ in the cooking liquor. In our study, this disadvantage could be compensated by a higher EA (+10 g/L) or H factor (+200), for reaching the same degree of delignification after SAQ and K pulping.

Figure 1 illustrates that delignification during SAQ-pulping was positively affected by the alkaline pre-extraction step. Lignin removal was favoured even in comparison with the kraft process, which agreed with the observations of other authors.[14,15] Zhang *et al.* observed lower kappa numbers after kraft- and soda-AQ-pulping of eucalypt wood treated with alkaline pre-extraction, even with a reduced alkali charge during pulping. Wafa Al-Dajani *et al.* monitored the total alkali consumption during kraft pulping and alkaline pre-treatment of aspen wood and noticed that less NaOH was consumed during the whole process when pre-extraction was carried out. Obviously, the alkali used for the degradation of hemicelluloses in a traditional kraft cooking was available for further delignification. In our study, 41.2% of the xylan in the original wood could be already extracted during the pre-treatment, while only 3.3% were removed during subsequent SAQ pulping. In a conventional kraft cooking, 38.6% of the total xylan was dissolved during pulping and evidently, their degradation reactions were competing with delignification. To reach the same kappa number after SAQ cooking, the H factor could be reduced by 200. Under conditions of alkaline pre-extraction, the wood structure opened up through swelling. This step served as a perfect impregnation, which might also accelerate delignification, being attributed to a very low amount of reject. The shive content was as low as for pulps after autohydrolysis alkaline pulping. In alkaline pulping of hardwood, the 4-Omehtyl-glucuronic acid (MeGlcA) side chains of xylan are partly transformed to hexenuronic acid (HexA), which renders the xylan more stable towards alkaline degradation. Eucalypt xylan is unusually rich in MeGlcA, which contributes to a high yield for eucalypt paper pulps.[26] On the other hand, HexA is responsible for the low efficiency of oxygen delignification of hardwood kraft pulps, contributes to the consumption of bleaching chemicals and unfavourably influences brightness reversion. For the production of dissolving pulps, the formation of substantial amounts of hexenuronic acid is a drawback of the alkaline cooking of eucalypt species. The HexA contents of the K and SAQ pulps as a function of the H-factor were high, no differences being observed between both processes (Fig 1). In contrast, alkaline extraction prior to SAQ pulping (E-SAQ) resulted in a substantial decrease in HexA formation, which confirmed the results of Zang *et al.*[15] This fact was quite comprehensible, because substantial amounts of xylan were removed during the pre-extraction step and, therefore, could not contribute to the formation of HexA. Additionally, the ratio of HexA to xylan in E-SAQ pulps (1.8) was lower than in SAQ pulps (2.1), which indicated that an early xylan removal impeded, to some extent, HexA formation during pulping.

Unbleached pulps

The concept of multifunctional alkaline cooking allows the manufacture of different pulp grades using the same core process for the delignification of either kraft (K) or soda-AQ (SAQ). On the basis of SAQ, a comparative evaluation of four different unbleached pulp grades comprising E-SAQ, SAQH, PH-SAQ and SAQ processes had been conducted, to elucidate the cell wall structure and the paper making properties. For completion, a kraft (K) and a PH-kraft pulp (PH-K), as well as a sulfite pulp (MgS), were added (Table 3).

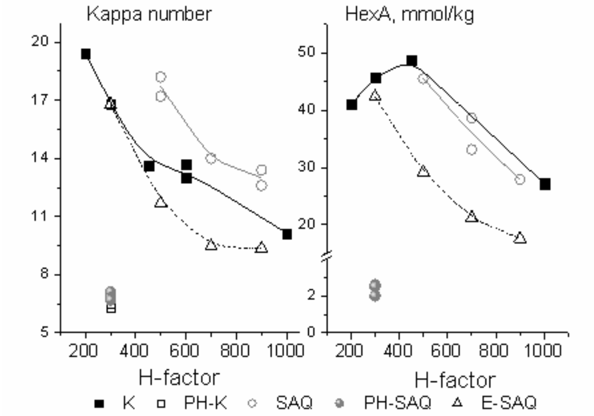

Figure 1: Kappa number and HexA content *versus* the H-factor for modified alkaline pulping

Table 3
Properties of unbleached eucalypt pulps from multifunctional alkaline pulping

Parameters	Unit	K	SAQ	E-SAQ	SAQH	PH-K	PH-SAQ	MgS
Kappa number	-	14.6	14.0	16.8	16.2	6.3	6.8	8.8
Viscosity	mL/g	1240	1115	1090	1160	1065	1125	900
Xylan	%	18.4	17.4	16.9	20.0	2.9	3.5	5.3
Tensile stiffness index at 30°SR	N*m/g	5.1	5.6	6.4	5.9	4.8	4.5	n. d.
Tear index at 30°SR	mN*m²/g	4.6	5.9	5.8	5.9	3.2	2.9	n. d.
Zero span unbeaten	kN/m	9.1	9.8	9.5	8.2	6.2	6.6	n. d.
Peeled xylan at 10% peel. mass	% odp	4.0	2.9	3.0	3.8	0.4	0.5	1.1

The beating performance could be classified into three categories (Fig. 2): the first category, including the PH-K and PH-SAQ pulps, required a high intensity of refining, due to the lack of hemicelluloses necessary for cross-linking, the second category of pulps, with moderate beatability, was represented by SAQ and E-SAQ pulps, and the third category of pulps, characterized by easy beatability and represented by K and SAQH pulps, showed the highest hemicellulose content. This was not only in coherence with the xylan content of the pulps, but also with its distribution on the cross-section of the cell wall. Figure 3 depicts the xylan to peeled mass after enzymatic peeling, a measure for xylan distribution over the transverse section of the cell wall. The same groups as for the beating experiments were visible. A high concentration of hemicellulose on the outer fibre wall was apparent for sulfite pulp, as demonstrated in previous studies.[22]

The sorption of xylan on fibres under alkaline cooking conditions was suggested to be a diffusion-controlled physical process. It seems to precipitate on the outermost fibre surfaces at low initial xylan concentrations while, with rising xylan concentrations, it subsequently penetrates the porous fibre wall to adsorb on the internal surfaces.[27] This may be applicable for the SAQH pulp which showed a xylan distribution on cross-section of the fibre almost exactly identical to the K pulp. No extensive re-deposition on the outer surface could be noticed. The adsorbed xylan in the SAQH pulp was evenly distributed throughout the cell wall, even if it obviously cannot be incorporated into the fibrils. The precipitation of xylan during the final phase of the kraft cooking could be excluded, due to the CBC pulping technique applied, which kept the pH high throughout the cooking step.

A clear correlation between a wide range of peeled xylan at 10% peeled mass with the tensile stiffness index and the elastic modulus at 4500 revolutions in the PFI mill could be established (Fig. 4). After intensive refining, these paper making properties were mainly influenced by the hemicellulose concentrations on the outer surface of the cell wall, which take part at the formation of fibre-fibre bonds.

All paper making properties of the three unbleached SAQ paper pulps were comparable to hardwood kraft pulps (Table 3).

The moderate beatability of the E-SAQ and SAQ pulp was consistent with a higher tear index.

On the other hand, the low intensity refining required by the kraft pulp corresponded to a lower tear index, which was in good agreement with literature data.[28] Molin *et al.* found out a lower tensile stiffness and tensile index, but a higher tear index, with a higher ratio of cellulose to hemicellulose in pulp after kraft pulping of spruce. The SAQH pulp showed both a low intensity refining and a high tear index. The slightly lower zero span for the SAQH pulp may be explained by the highest xylan content of all tested pulps.

Under the conditions selected for our studies, the alkaline pre-extraction of hemicelluloses did not affect unfavorably the paper making qualities.

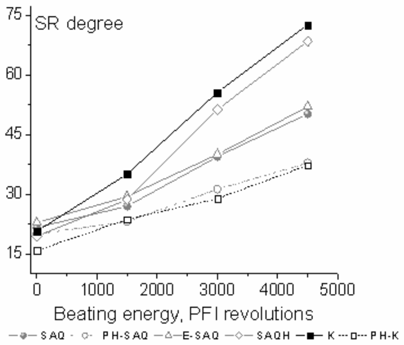

Figure 2: Freeness in ºSR as a function of beating energy in terms of PFI revolutions for *Eucalyptus globulus* pulps

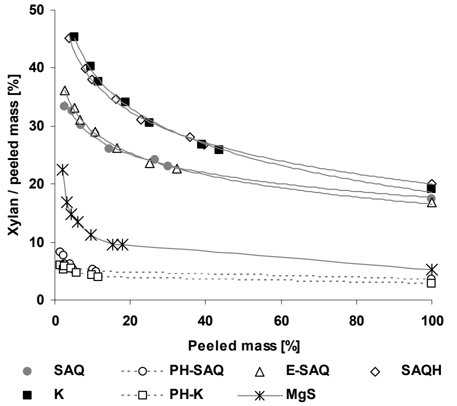

Figure 3: Enzymatic peeling of pulps from *Eucalyptus globulus* after multifunctional alkaline pulping

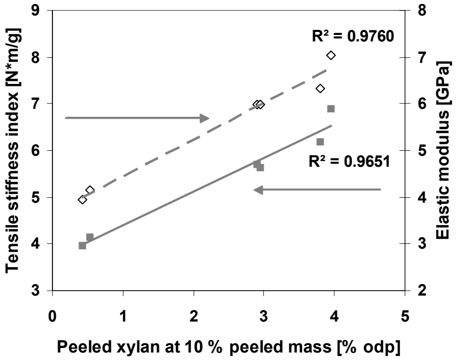

Figure 4: Tensile stiffness index and elastic modulus beaten at 4500 revolutions in the PFI mill as a function of surface xylan of unbleached eucalypt pulps

In contrast, the E-SAQ pulp showed an unexpected high tensile stiffness, in spite of the lowest hemicellulose content. Taking into account sheet density, this effect was still valuable, which was surprising and has to be confirmed in further trials.

It has to be stated that the cell wall structure of the dissolving pulps originating from autohydrolysis alkaline pulping is different in paper pulps, because the primary (PW) and secondary wall 1 (S1) are almost completely removed after cooking. Obviously, the low values for zero span, tear and tensile index cannot be only correlated first with the surface xylan. They must be also attributed to the differences in the mechanical properties of the secondary wall 2 (S2), due to longitudinal and more parallel oriented microfibrils, embrittlement of the wall because of the low xylan content and irreversible collapse of the lumen.

Oxygen bleaching and CCE-stage

All pulps were subjected to a standard oxygen delignification step. Paper pulps with matchable levels of residual lignin were selected for bleaching. After oxygen delignification, the K, SAQ and E-SAQ pulps were divided into two series for the final bleaching: one series with CCE, for the production of dissolving pulps, and another without CCE, for paper pulps.

The results of pulping, oxygen delignification and alkaline post-extraction are shown in Table 4.

Table 4
Characterization of *Eucalyptus globulus* pulps after pulping, O-delignification and CCE-stage

	Total yield, % odw	Kappa number	Brightness, % ISO	Viscosity, mL/g	Xylan, % odp	R18, %	HexA, µmol/g
K	50.6	14.6	40.8	1375	18.1	92.0	40.7
K-O	49.9	9.8	60.0	1140	18.6	91.5	38.1
K-O-CCE	40.8	4.9	64.6	1355	4.0	98.5	9.2
SAQ	51.1	15.5	39.7	1110	19.4	94.7	39.1
SAQ-O	50.7	10.3	54.4	1010	19.2	94.0	40.9
SAQ-O-CCE	43.3	6.2	57.9	1120	6.7	98.4	15.5
E-SAQ	50.6	15.7	37.4	1100	18.3	95.2	39.9
E-SAQ-O	50.1	10.4	51.0	965	15.3	94.8	38.4
E-SAQ-O-CCE	43.0	6.4	53.9	1070	6.5	98.5	14.7
PH-K	37.4	5.8	43.4	995	2.8	97.2	n. d.
PH-K-O	37.2	2.5	62.7	880	2.7	97.3	4.0
PH-SAQ	36.9	6.3	47.7	1090	4.5	96.7	2.3
PH-SAQ-O	36.6	3.0	63.9	950	3.6	96.7	4.1
MgS	45.9	8.8	59.3	900	5.3	91.4	n. d.
MgS-O	40.6	3.9	77.5	850	4.2	92.8	2.6

Total yield was quite comparable for both cooking concepts, K and SAQ, which agreed with the results obtained by other authors.[24] After the CCE-treatment, the differences in yield corresponded to the differences in the xylan content, because the standard bleaching parameters were optimised for the kraft pulp. Alkaline pre-extraction, however, resulted in a slightly lower yield after pulping with increasing H-factor, compared to the reference pulping processes. This was in good agreement with the lower xylan contents, of about 2%, of unbleached pulp, and may be attributed to the pre-extraction with concentrated sodium hydroxide at moderate temperature. Nevertheless, after the O- and CCE-stages, the yields of the K-, SAQ- and E-SAQ pulps were in the same range.

No differences in pulp yield at a given kappa number and delignification rate between PH-SAQ and PH-K pulps were observed (Table 4), which agreed with the published literature.[29] The former showed a slightly higher R18 and a lower xylan content than the latter. This difference may be attributed to the efficient stabilizing effect of AQ in SAQ pulping. Table 4 also depicts the low level of yields of autohydrolyzed pulps, compared to alkaline pulping with post-extraction. Even after the first bleaching steps, the yields were distinctly lower, although a significant yield loss was observed after alkaline purification (CCE) of the paper pulps. This indicated that a considerable amount of cellulose was lost during PH-K and PH-SAQ cooking. Briefly, our studies verified a yield advantage for post-extracted pulps, of 4 to 6% odw, in comparison with prehydrolysed dissolving pulps (Table 4).

It is well-established that hardwood xylan precipitates on pulp fibres during kraft pulping.[30] The determining factors are temperature, NaOH concentration and hemicellulose concentration in the cooking liquor. Most of these studies were conducted with birch xylan, under conditions of kraft pulping.[27] The chemical structure and composition of xylan from *Betula pendula* are significantly different from eucalypt xylan.[26, 31] In a previous work, the effect of temperature and NaOH concentration on the sorption of eucalypt kraft xylan from CCE during kraft pulping was investigated.[32] The resulting adsorption isotherms showed that higher temperatures and lower EA favoured re-precipitation of xylan.

In this study, the effect of CCE-lye as an alkali source on SAQ cooking had been investigated in some preliminary tests, by applying the CBC cooking concept. Although the impregnation and cooking liquors were not yet at equilibrium, the addition of xylan containing lye clearly contributed to higher pulp yields, due to an increase in the xylan content. The uptake of xylan corresponded to 3.6% on oven dry wood after SAQH cooking.

Previous studies[27,33] showed that the adsorbed xylan is multilayered, not aligned with the microfibrils and even aggregated, as well as difficult to remove with NaOH. This xylan may act as a physical or chemical barrier towards further delignification. Under the conditions of our investigations, no hindrance in lignin removal during oxygen bleaching could be noticed. While the SAQH pulp showed a kappa number reduction of 70%, the kappa number of the K, SAQ and E-SAQ pulps declined by 66 to 67% (Table 4).

After cooking, the brightness levels of the kraft and SAQ pulp were in the same range. Nevertheless, the SAQ pulp showed a poorer brightness increase during oxygen bleaching. Bose *et al.*,[34] who described this phenomenon, found out a higher content of more condensed structures in the residual lignin from the non-sulfur process than from kraft pulping. In the SAQ delignification mechanism, the formation of coniferyl alcohol is 4 to 5 times higher than in kraft pulping. The degradation products are thus responsible[35] for the formation of condensation products and finally for the lower brightness increase of the SAQ pulps. The lower brightness was consistent in our studies for SAQ, E-SAQ and SAQH pulps. For prehydrolysis kraft and prehydrolysis SAQ pulps, no differences in brightness and in residual lignin could be observed after the O-stage.

For all three post-extracted SAQ pulps, the HexA content of residual xylan in the pulp was raised after oxygen delignification from 2.0 to 2.1 for the SAQ, to 2.2 for the E-SAQ and to 2.5, respectively, for the SAQH pulp. At the same time, the HexA-to-xylan ratio for kraft pulp declined from 2.2 to 2.0. Evidently, due to a higher degree of non-stabilized xylan in the oxygen bleached kraft pulp, 83% of the xylan could be removed with an alkaline post-extraction step, while only 70% of the SAQ and 63% of the E-SAQ xylan were eliminated from the pulp. Therefore, the xylan contents of the SAQ and E-SAQ pulps (6.7 and 6.5%) were high for their application as dissolving pulps. The standard CCE was optimised for the kraft pulp and could be adjusted to the requirements of the SAQ pulps, because of a probably different structure of the residual xylan.

A second reason for the different behaviour of the SAQ pulps may be a broader molecular weight distribution of the xylan, with an increased part of the high molecular weight hemicelluloses, due to the stabilising effect of the AQ (Fig. 5). This fact may also explain the unexpected high R18 of the SAQ pulps after cooking and O-bleaching (Table 4).

Figure 5 also depicts the effect of xylan adsorption during SAQH and xylan removal during E-SAQ pulping. As expected, the MgS pulp showed a high fraction of low molecular weight carbohydrates, whereas the prehydrolysed pulp exhibited a low content of low molecular weight hemicelluloses.

Membrane separation

The cost-effective separation and purification of the alkali-extracted hemicelluloses is a prerequisite to establish economically viable biorefinery concepts. The technology of choice is a pressure-driven membrane separation process, such as ultra- or nanofiltration.

For demonstration, bench-scale experiments had been conducted, with CCE lye from a commercial TCF bleached eucalypt kraft pulp as a feed substrate. Due to an average molecular weight of the extracted xylan of about 15 kDa, the use of ultrafiltration membranes assured high efficiency and selectivity. The paper pulp was subjected to a standard CCE stage, resulting in CCE lye with a NaOH concentration of 79 g/L and a hemi concentration of 18 g/L. Density was of 1.10 g/cm^3 and dynamic viscosity was of 3.49 mPas.

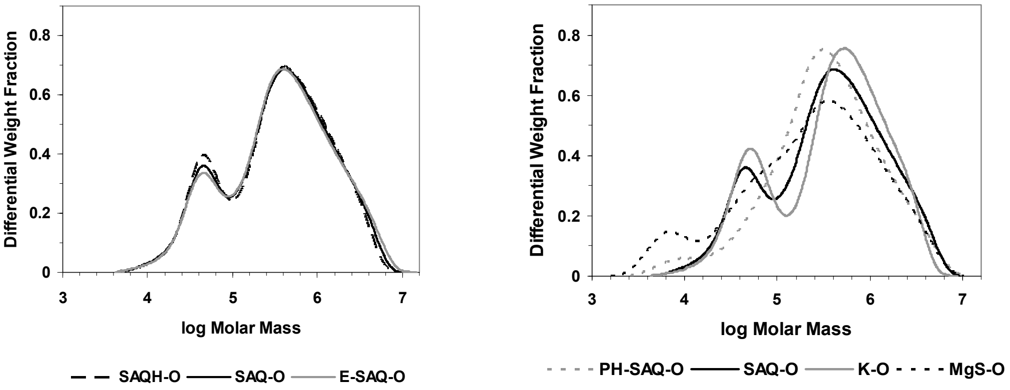

Figure 5: Molecular mass distribution of SAQ, E-SAQ, SAQH pulps and PH-SAQ, SAQ, K and MgS pulps after oxygen delignification

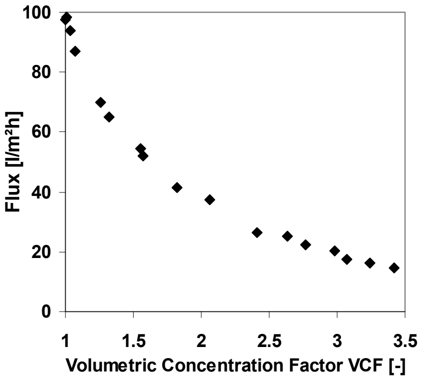

Figure 6: Performance of ultrafiltration of CCE-lye from a commercial TCF bleached *Eucalyptus globulus* kraft pulp

The ultrafiltration set-up in the concentration mode allowed a VCF of 3.0 at a reasonably high flux of up to 20 $Lm^{-2}h^{-1}$ (Fig. 6). The ratio of hemi-to-NaOH in the feed of 0.23 could be raised to 0.67, resulting in a 96.9% yield. It may be further increased by a subsequent diafiltration process, to improve the economic feasibility of xylan precipitation and purification.

CONCLUSIONS

The present study confirmed the suitability of the multifunctional alkaline pulping concept to soda-AQ cooking. Pre- and post-treatments to sulfur-free alkaline pulping allowed the production of modified paper and dissolving pulps with promising properties. The chemical structure of the extracted hemicelluloses was largely preserved, constituting a valuable source for the conversion to sugar-based products.

1. Sulfur could be successfully replaced by anthraquinone. The performance of soda-AQ cooking was quite comparable to that of kraft cooking. As expected, the paper making properties of the SAQ pulp were slightly inferior to those of the kraft pulp. No differences in processability and pulp properties between prehydrolysis soda-AQ and prehydrolysis kraft pulping were observed.
2. Alkaline post-extraction resulted in a 4 to 6% higher yield over prehydrolysis alkaline pulping. Contrary to autohydrolysis, alkaline pre-extraction showed only a minor effect on pulp yield, accelerated the delignification rate and lowered HexA formation.
3. The use of CCE-lye as an alkali source for soda-AQ pulping clearly contributed to higher pulp yields, as due to xylan sorption. The resulting paper making properties were in the range of a hemicellulose-rich hardwood kraft pulp.
4. Efficient separation of xylan from strong alkaline solutions through ultrafiltration was demonstrated in bench-scale experiments. A reasonably high flux could be maintained even at high volumetric concentration factors.

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