Progress and Challenges in the Isolation of Xylan from Eucalyptus Wood

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Abstract

There is an increasing interest in utilizing xylan from hardwood in the food and non-food area. The liberation of xylan from the cell wall matrix of wood is, however, highly restricted by the strong interactions with the lignin network. Xylan stability against alkaline pulping is particularly high in *Eucalyptus globulus* owing to its peculiar structure containing galactosyl and glucosyl units attached at *O*-2 of 4-*O*-methyl-α-D-glucuronic acid (MeGlcA).

Nevertheless, alkaline pulping constitutes a suitable platform for the selective and efficient separation of xylan from cellulose and lignin. The use of *Eucalytpusglobulus* allows the entire replacement of hydrogen sulfide by anthraquinone in the cooking liquor during the delignification part of wood fractionation, which greatly facilitates the isolation of separated lignin and hemicelluloses fractions. More than 30% of the wood xylan can be isolated as polymer in relatively high purity by pre-alkaline extraction applying appropriate conditions, while subsequent alkaline pulping exertsonly a minor effect on pulp yield. The xylan yield may be increased to more than 60% by combining pre-alkaline extraction with cold alkaline post-extraction. The resulting hemicellulose-lean pulp constitutes a novel generation of dissolving pulps.

Autohydrolysis prior to alkaline cooking represents a reliable concept to separate xylan, predominantly in oligomeric form, provided that lignin precipitation can be kept under control. The direct formation of monomeric xylose was accomplished by the addition of sulphuric acid or oxalic acid as catalysts which favour the cleavage of the glycosidic bonds of the xylo-oligosaccharides rather than dehydration and other side reactions. In contrast to neutral or alkaline pretreatments, acid pretreatments of wood render the remaining carbohydrate fraction very vulnerable against alkaline post-treatments such as kraft or soda-anthraquinone (SAQ) pulping.

Keywords: eucalyptus; prehydrolysis; biorefineries; hemicelluloses; dissolving and paper grade pulps.

Introduction

Hemicelluloses are important cell wall components being associated with cellulose microfibrils and the lignin matrix. In hardwoods they constitute almost one third of the total organic material present with O-acetyl-(4-O-methylglucurono)xylan as the major component. There is an increasing interest in the application potential of xylan polymers isolated from wood and non-wood sources both in the food and non-food area. The liberation of the xylan component from the cell wall matrix of wood, however, is restricted by the strong interactions with the lignin network. In addition, extensive hydrogen bonding between xylan and cellulose impedes the isolation of xylanwithout any structural and chemical alterations [1].

In common pulping operations, xylan is only partly preserved as a polymer forming a network with cellulose. Owing to the high alkali resistance of xylan, hardwood kraft pulps contain between 50 and 60% of the wood xylan, but only 25% of the wood xylan is retained in acid sulfite paper pulps [2]. The other part of the wood xylan is converted into a variety of different hydroxyacids under alkaline pulping conditions whereas during acid sulfite cooking the greatest part of the wood xylan is hydrolyzed into acetic acid and monomeric xylose.

Alkaline pulping constitutes a suitable platform for the selective and efficient lignin removal [2]. The use of hardwood allows the entire replacement of hydrogen sulfide by anthraquinone (AQ) in the cooking liquor during the delignification part of wood fractionation. Two pre-treatments and one post-treatment to Soda-AQ (SAQ) pulping of *Eucalyptus globulus* were studied with respect to the separation of xylan as polymer, oligo- and monomer. At the same time a complete balance of all wood constituents has been accomplished, which allows the evaluation of the selectivity of the single fractionation processes.

It has been shown that about 25% of the wood xylan can be isolated by pre-alkaline extraction (E) as a high molecular weight polymer using appropriate conditions [3]. Owing to the absence of a strong nucleophile, the xylan separated from the pre-alkaline extract by ultrafiltration and subsequent precipitation in a non-solvent reveals an astonishingly low lignin contamination [2]. Interestingly, the subsequent SAQ

pulping operation has practically no adverse effect on pulp yield [2, 3]. Thus, the combined E-SAQ process decreases the overall conversion rate of xylan into hydroxyacids substantially. As reported previously, the overall xylan yield may be further increased by an alkaline post-extraction (CCE) following an E-SAQ procedure [2]. The resulting hemicellulose-lean pulp constitutes a novel generation of dissolving pulps.

Autohydrolysis treatment prior to SAQ cooking is known to separate the hemicelluloses efficiently from the other wood polymers by hydrolytic cleavage of the glycosidic bonds catalysed by the released acetic acid [5]. Xylan is fragmented into water soluble polymeric and oligomeric fractions. The formation of monomeric xylose, however, requires high P-factors which in turn favors the formation of undefined degradation products through consecutive reactions [1, 4]. The generation of monomeric xylose at lower intensity can be accelerated by the addition of strong acids. Sulphuric acid and oxalic acid were selected as catalysts to promote the acid hydrolysis of hemicelluloses.

The aim of this study was to comparatively evaluate water autohydrolysis, acid-catalyzed hydrolysis and alkaline extraction of *Eucalyptus globulus* with reference to their potential of manufacturing xylan-derived products of high value. Further, the removal of xylan from the pulp by a CCE treatment to produce a novel generation of dissolving pulp was thoroughly investigated.

Experimental

Intensity of autohydrolysis

The intensity of autohydrolysis is conveniently expressed as P-factor using an Arrhenius-type of expression [6]. A value of 125.6 kJ mol^{-1} for the fast-reacting xylan (X_F), based on extensive investigations of xylan hydrolysis from *Eucalyptus saligna*, has been suggested for the P-factor (P-X_F) calculation in a prehydrolysiskraft pulp mill [7]. Overend and Chornet introduced the severity factor, R_0, to quantify the intensity of hydrothermal biomass treatment using the following expression [8]:

$$R_0 = t \cdot exp \left(\frac{T-100}{14.75} \right) \tag{1}$$

wheret is the residence time in minutes and T the reaction temperature measured in ⁰C. The logarithmic plot of R_0 allows the illustration of the data in a more condensed form. The amounts of released components during autohydrolysis are, however, more precisely predicted by the P-factor than with the severity factor R_0. To account for the addition of catalysts such as sulphuric acid and oxalic acid equation (1) the initial proton concentration in the pre-treatment was considered according to equation (2) [9]:

$$R_0^{'} = R_0 \cdot [H^+] = log(R_0) - pH \tag{2}$$

Wood chips

*Eucalyptus globulus*wood chips from plantations in Uruguay were used for kraft pulping experiments after a laboratory screening according to standard method SCAN CM 40:94. The average characteristics of the screened wood chips were as follows: 22.7% Klason lignin (KL) (TAPPI test method T 222 om-98), 4.7% acid soluble lignin (TAPPI test method T om-250), 42.4% cellulose (C), 2.2% glucomannan (GM), 17% xylan assuming that 60% of the linkages between 4-*O*-methylglucuronic acid (MGA) and the xylan backbone survive the primary and secondary hydrolysis step [13], 0.4% arabinan, 0.1% rhamnan, 4.8% total uronic acids (2.4% MGA, 1.9% galacturonic acid and 0.5% glucuronic acid), 0.6% acetone extractives, and 0.4% ash (methods T 211 om-93; ISO 14453:1997). The moisture content was 31.6%.

Prehydrolysis

The chips were ground with a Retsch-type grinding mill and fractionated. The fraction with particle sizes between 2.5 and 3.5 mm was collected and used both for autohydrolysis and acid-catalysed hydrolysis.The experiments were carried out in a lab-scale Parr reactor station with mechanical stirring and a volume of 450ml. 50g of wood were placed inside the reactor together with enough deionized water to reach a liquor-to-wood ratio of 5:1. After fast heating-up to the preset temperature it was maintained until the desired P-factor was reached. Acid catalysis was achieved by the addition of sulphuric acid (0.01 – 0.1 M), oxalic acid (0.01 – 0.1 M) and acetic acid (0.02 – 0.15 M). The latter was chosen as a comparison to autohydrolysis. Subsequently, the prehydrolysate was separated from the wood residue by displacement with nitrogen to a preheated, second reactor containing saturated steam with the hydrolysis temperature. During this separation step no temperature and pressure drop occurred. The aim of this isothermal phase separation was to recover all compounds dissolved in the hot prehydrolysate, particularly those which are insoluble at lower temperatures. From selected autohydrolysates, xylan was precipitated by the addition of ethanol in

avolumetric ratio of 8:1. The generated precipitate after 48 h in the refrigerator was centrifuged, dissolved in water and finally freeze-dried.

Alkaline pre-extraction of wood

Alkaline pre-extraction of the wood particles was carried out in the lab-scale Parr reactor previously described. As extractants both white liquor with a sulfidity of 25% and a sodium hydroxide solution with a causticity of 85% and an AQ content of 0.5 g/L were utilized. Xylan removal efficiency and selectivity was optimized using a fixed alkali concentration of 2.5 mol/L considering the moisture content at temperatures 30ºC, 60 ºC and 90ºC, while the extraction time and the liquor-to-wood ratio were kept constant at 30 min and 5:1 g/g, ºC respectively. After each trial the wood chips were thoroughly washed with cold deionized water to leach out the entrapped alkaline liquor. The extract was concentrated by ultrafiltration (UF). The concentrated xylan was precipitated by adjusting the pH with sulphuric acid to about 3.

Alkaline post-extraction of a TCF bleached *Eucalyptus globulus*kraft pulp

Xylan was extracted by cold caustic extraction (CCE) followed by precipitation in sulfuric acid (Table 1). Further refining of the xylan consisted of centrifuge washing, dialysis and freeze-drying.

Membrane filtration

The laboratory-scale filtration equipment Memcell from KCS Osmota equipped with a plunger pump was used for the ultrafiltration of the hemi-enriched lyes.

The ultrafiltration membrane UP010 from Microdyn-Nadir was applied in the flat-sheet crossflow cell with a 44 mil parallel spacer resulting in an active membrane area of 80 cm². The cut-off of this alkali stable polyethersulfon membrane is 10 kDa. The temperature was kept constant at 40 °C by heating the 7L-feed-vessel. The pressure before the membrane was varied between 200 and 800 kPa. The applied flow rate was in the range of 1 to 3 L/min. Two process modes were applied. The permeate was collected in a separate container during the concentration mode.

Molar mass distribution of hemicelluloses

Molecular mass distribution was obtained by size exclusion chromatography with RI detection and 0.5 M NaOH as eluent. The system consisted of a pre-column (MCX 1000, 10µ, 8 * 50 mm, PSS, Germany) and two analytical columns (PSS MCX 1000, 10µ, 8 * 300 mm, PSS, Germany). The calibration standards: xylose (Merck, Germany), cellobiose, maltotriose, stachyose (Fluka), dextran (PSS, Germany): 1350, 5200, 11600, 23800, 48600, and pullulan (Showa Denko): 5900, 11800, 22800, 47300, 112000, 212000, 404000.

Carbohydrate analysis

The neutral sugar monomers were determined by anion exchange chromatography with pulsed amperometric (PAD) detection after total hydrolysis with H_2SO_4 according to [10].

Results and Discussion

SAQ pulping constitutes a suitable platform for the selective and efficient delignification of hardwoods. At the same time, however, a concomitant degradation of almost 50% of the hemicelluloses to hydroxyacids takes place. The hemicelluloses may be pre-extracted prior to SAQ pulping either by pre-hydrolysis or pre-alkaline extraction to increase the overall yield of hemicelluloses as monomers, oligomers and polymers (Figure 1). In this study, these two pre-treatments of *Eucalyptus globulus* prior to SAQ pulping have been thoroughly investigated. Further, a commercial TCF bleached *Eucalyptus globulus*kraft pulp was subjected to CCE to selectively isolate the xylan as a pure polymer. This post-treatment may be conveniently integrated into the fiber line, preferably between oxygen delignification *and* bleaching to ensure high efficiency of washing and chemical recovery.
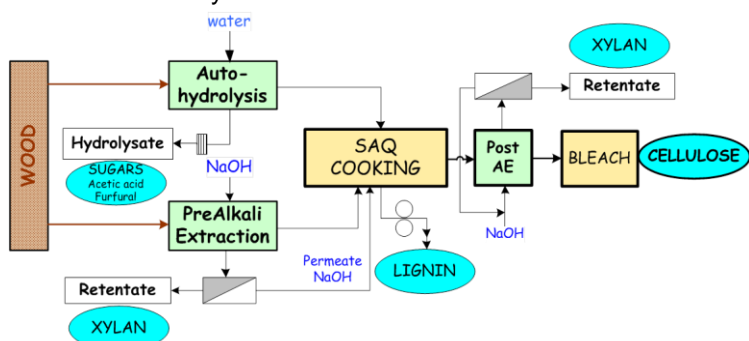

Figure 1:   Sulfur-free biorefinery concept to simultaneously recover the hardwood polymers in high purity and yield.

Prehydrolysis of *Eucalyptus globulus*

Figure 2aconfirms a rather accurate relationship between the wood yield and the severity factor accounting for the initial acidity (equation 2) of the sulfuric acid and oxalic acid catalyzed hydrolysis of *Eucalyptus globulus*. Surprisingly, the relationship is more significant when the initial proton concentration and not the final proton concentration is taken into account.In this way the wood yield losses can be related to the intensity of prehydrolysis treatments using strong to medium-strong acids ($pK_a < 3$). The yield losses of birch through oxalic acid-catalysed hydrolysis show a similar dependency on the reaction severity asfor eucalyptus. This observation indicatesthat the wood solubilization mechanisms initiated by acid catalysis are largely independent from thewood species. To allow a more reliable reasoning more work has to be done.
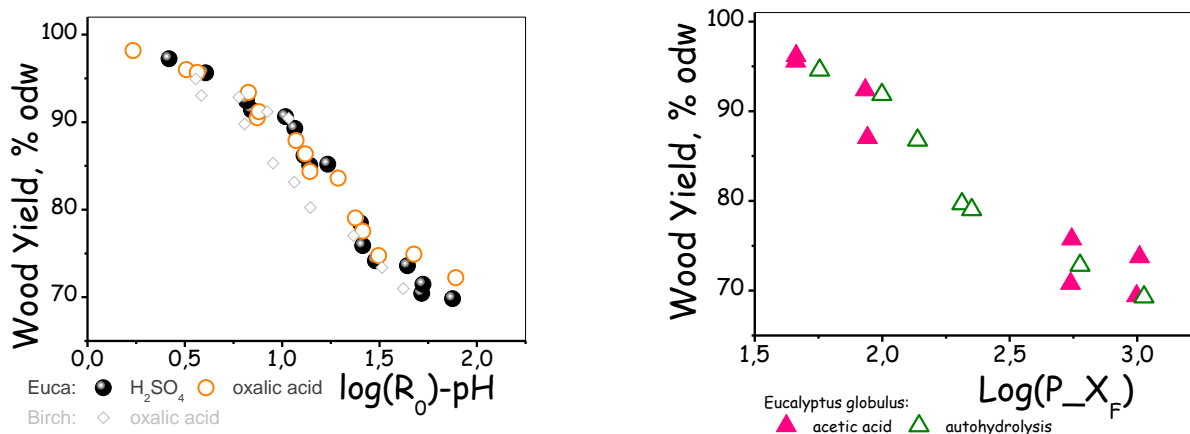

Figure 2a: Wood yield versus severity factor accounting for the initial pH of the sulfuric acid- and oxalic acid-catalyzed hydrolysis. 2b: Wood yield versus the logarithm of the P-factor of water autohydrolysis with and without the addition of acetic acid.

Unfortunately, the severity expression of equation 2 is not well suited to describe the wood yield losses of autohydrolysis reactions. This behavior might be explained by the oberservations of Skrabal who found that the hydrolysis of certain ethers exhibits a pH-independent region in addition to its dependency on $[H^+]$ and $[OH^-]$ [11].Skrabal called this type of process a "water reaction" which was changed to hydrothermolysis by Bobleter many years later [1]. This reaction is characterized by the addition of water only and the subsequent direct formation of monosugars in which the change in $[H^+]$ in $[OH^-]$ does not alter the reaction constant.
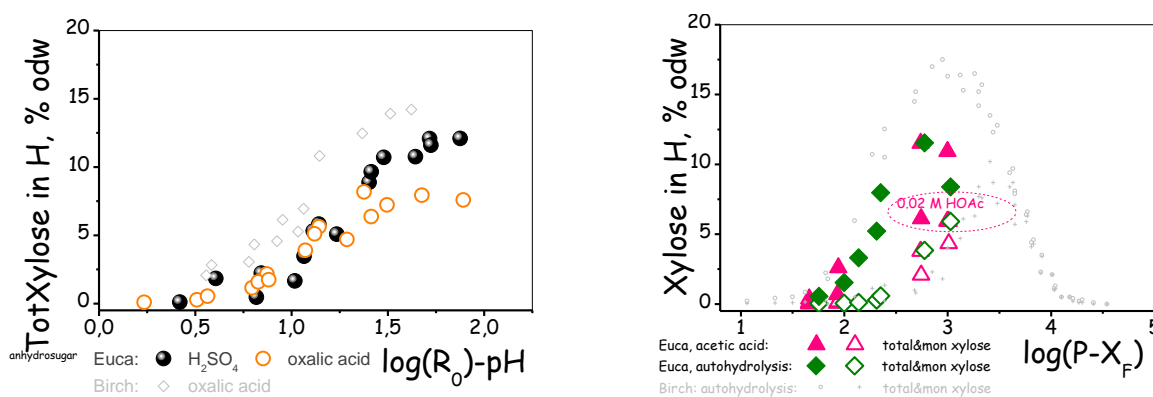

Figure 3a: Yield of the total amount of released xylose during acid-catalysed hydrolysis as a function of the severity factor accounting for the initial pH.3b: Yield of total amount of liberated xylose during autohydrolysis as a function of $log(P-X_F)$.

The release of xylose during acid-catalysed hydrolysis follows a two-step reaction with a slow initial and a fast second phase (Figure 3a). Apart from a few results at the highest intensity, oxalic acid and sulphuric acid-catalysed prehydrolysis show a comparable xylose liberationpattern. The maximum amount of total xylose in the hydrolysate constitutes about 11.6% (anhydroxylose) on odw which denotes 68% of the xylan content in wood. This is about the same ratio as determined for the oxalic acid-catalysed hydrolysis of birch wood. However, there, the maximum amount of removed xylose seems not been reached yet (Fig 3a).For the hydrothermal treatment of birch wood it was shown that the amount of recovered xylose follows a

log normal-shaped curve as a function of the intensity peaking at alog(P-X_F) value of about 3 (Figure 3b). The few results on the hydrothermolysisof *Eucalyptus globulus* confirm this reaction pattern also for this wood species. However, more experiments are needed at higher log(P-X_F)-intensities to identify the maximum yield of xylose in the hydrolysate as well as the shape of the xylose degradation curve.

The hydrolysis rate of solid xylan slightly decelerates at a log(P-X_F) higher than 2.5 owing to an increased generation of monomeric xylose through the hydrolytic cleavage of oligomers.However, the hydrothermal treatment of wood isnot aprofitable source for the recovery of monomeric sugars.As indicated in Figure 3b for birch wood, the hydrolytic cleavage of oligomeric xylose competes with degradation reactions, particularly to furfural via dehydration reactions [12].Sulphuric acid-catalysed hydrolysis allows the complete conversion of the released xylose to monomeric xylose as depicted in Figure 4a. The final yield of monomeric xylose reaches about 13% on odw which equals a ratio of 75% of the total wood xylan. Oxalic acid catalysis is significantly less efficient in the generation of monomeric xylose which is in clear contradiction to the results obtained from oxalic acid-catalysed prehydrolysis of birch wood (Figure 4a).More experiments are necessary to draw a final conclusion. As already indicated, xylose is liberated in polymeric and oligomeric form during the initial phase of autohydrolysis. With increasing intensity xylo-oligosaccharides are hydrolysed to monomers which are further convertedto furfural and other compounds following complex, consecutive reaction patterns.
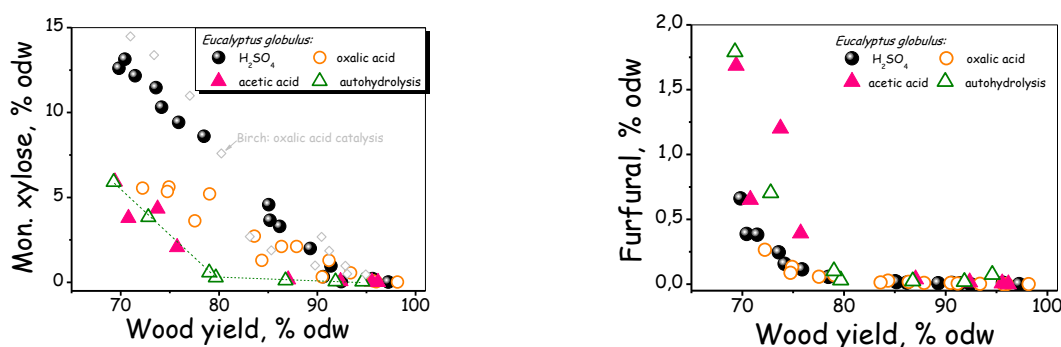

Figure 4a: Monomeric xylose yield (as anhydro sugar) as a function of wood yield for acid-catalysed hydrolysis and autohydrolysis treatments of Eucalyptus globulus. 4b: Furfural formation versus wood yield for acid-catalysed hydrolysis and autohydrolysis treatments of Eucalyptus globulus.

Figure 4b exemplifies the difference between acid-catalysed and hydrothermal wood treatments with regard to the generation of furfural. While the dehydration rate to furfural is very low and thus comparable for both processes until a wood yield of about 80% is achieved, it increases more rapidly during progressive treatment intensities for autohydrolysis as compared to acid-catalysed prehydrolysis and reaches 1.7% and 0.7% of furfural at a wood yield of 70%, respectively.

Another important side reaction during hydrothermolysis is the degradation of lignin structures mainly related to the acid soluble lignin [13]. Lignin is fragmented into low molecular fractions with a high content of phenolic groups and other reactive structural features.The hydrophobic lignin forms a dispersed particle solution in the acidic hydrolysate. To distinguish between the particle sizes of the dispersed lignin molecules the hydrolysate was filtrated through a 0.45 μm membrane filter. The filtrated part of the lignin was denoted as "soluble", the rest as "insoluble" lignin.Figure 5a demonstrates that the amount of soluble lignin increases with rising prehydrolysis intensity, while the amount of insoluble lignin stays relatively constant at about 0.6% on odw with a very large standard deviation. This is mainly true for the acid-catalysed hydrolysis treatment. Hydrothermal treatment, however, initiates a significant increase also of the insoluble lignin when the intensity is raised, representing wood yield losses from 20 to 30% (Figure 5b).This discrepancy to the acid-catalysed prehydrolysis may be explained by a slight shift of the lignin degradation mechanisms from heterolytic cleavage of beta-ether linkages (via benzyliccarbocations) during moderately acid and strong acid conditions to partly homolytic cleavageduring hydrothermal treatment [14]. The resulting radical intermediates may undergo coupling reactions forming high molecular weight condensed structures [13]. The formation of these insoluble, sticky lignin-derived precipitates is one of the major obstacles to commercialize the water prehydrolysis treatment of wood [15].
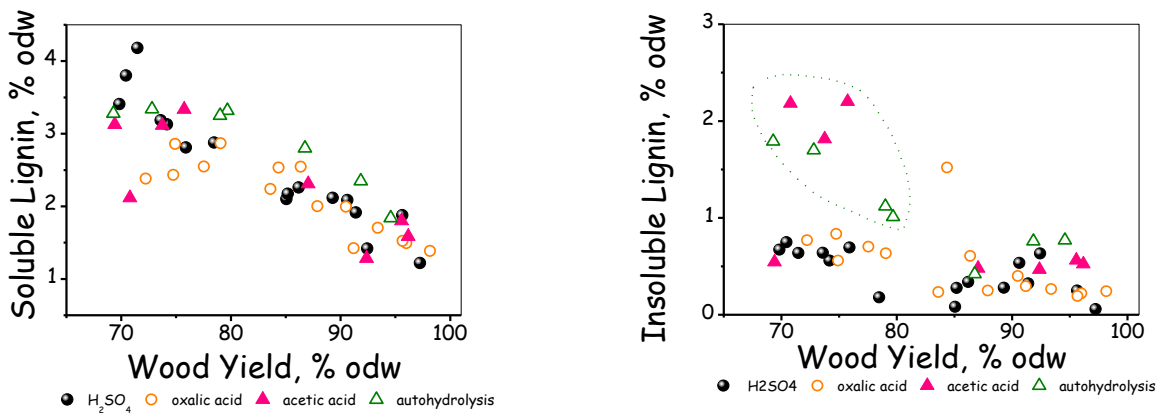
Figure 5: Amount of soluble (a) and insoluble lignin (b) in the hydrolysate as a function of wood yield of acid-catalysed and autohydrolysed Eucalyptus globulus.

Alkaline pre-extraction

The aim is to remove great parts of the xylan fraction from wood which is degraded during alkaline cooking. At the same time the extract should contain a minimum amount of lignin to facilitate the purification of the removed xylan. This requirement can be accomplished fairly well when the alkali source is pure caustic instead of white liquor (Fig 6b). The absence of a strong nucleophile, such as hydrogen sulphide, favors the removal of xylan over lignin.Preliminary trials revealed optimum extraction conditions at a caustic concentration of about 2.5 M and a temperature of about 90°C as demonstrated in Figure 6. The results are very comparable to those recently obtained on birch wood [16].
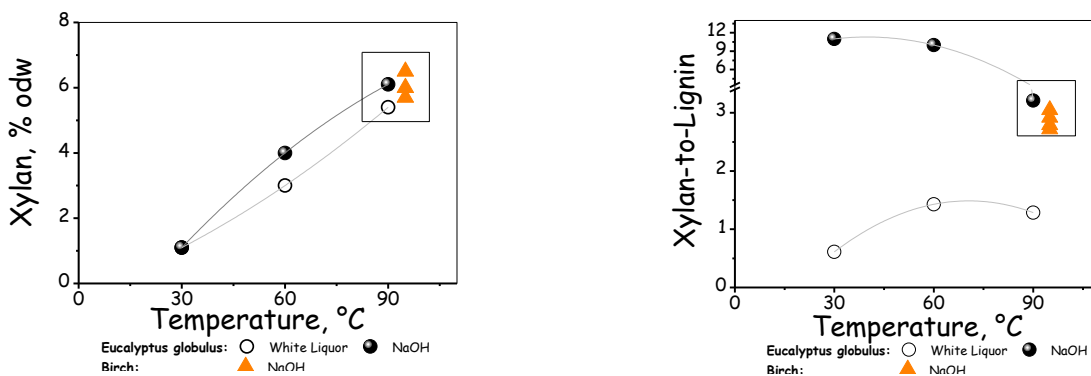

Figure 6: The amount of extracted xylan (left) and the xylan-to-lignin ratio (right) from Betula p. as a function of NaOH concentration, temperature and chip size dimensions.

It is suggested to realize alkaline pre-extraction in mill scale according to the continuous batch system outlined in Figure 7. Pure caustic is pumped from an E-lye tank through the digester from bottom to top until the desired hemi dissolution has been achieved. In parallel, this treatment serves as an intensified impregnation step. Subsequently, the cooking process starts once the hemi-enriched E-lye has been displaced by the cooking liquor. The dissolved xylan is further concentrated by ultrafiltration followed by diafiltration where the dilution factor is adjusted according to the final use of the xylan.The permeate, which contains the hemi-lean caustic solution contaminated by low molecular lignin fractions, is recycled to the cooking stage.

The xylan concentrated in the diafiltrationretentate should have both high xylan-to-lignin and high xylan-to-caustic ratios to facilitate subsequent precipitation and purification procedures. In case of a paper grade production facility the retentate could be utilized as alkali source for oxygen delignification. In this way practically all the xylan precipitates onto the pulp fiber surface owing to a low caustic concentration in the oxygen delignification tower. Preliminary estimates show that about 5% of high molecular E-xylan on odw can be recycled to the E-SAQ pulp which contributes to a 3-4% higher final pulp yield as compared to the SAQ reference case.
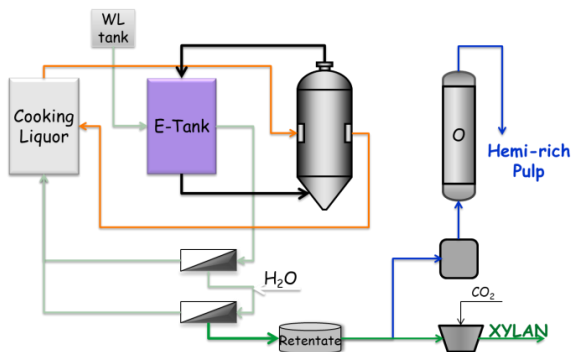
Figure 7: Simplified scheme of alkaline pre-extraction of wood.

Alternatively, xylan can be isolated from the retentate as a polymer by the addition of a non-solvent. The shift of the pH to 10 or lower by the addition of an acid (CO_2, mineral acid)has been proven to inducexylan precipitation with the disadvantage that the caustic solution is converted to a salt solution which has to be recycled to the recovery. The addition of an alcohol as a non-solvent preserves the sodium hydroxide solution for reuse. The necessary alcohol recovery is, however, energy intensive and requires high investment costs.

Alkaline post-extraction

A simple cold caustic extraction of a paper grade kraft pulp allows the manufacture of a novel generation of dissolving pulps [2]. This type of pulp seems to be particularly suited for the conversion to regenerated cellulosic products using the Lyocell-type process. The alkaline extraction may be accomplished in any step after cooking or bleaching. For the sake of simplicity we subjected a commercial TCF bleached *Eucalyptus globuluskraft* pulp from ENCE to a CCE treatment. A simplified mass balance of this process is depicted in Table 1.

Table 1:*Conditions and outcomeofa CCE treatment of a TCF-bleached Eucalyptuskraft pulp from ENCE. Modifiedfrom [2].*

Parameter	Unit	PULP K	Lye	filtrate	PULP K-CCE
			CCE-treatment		
CCE					
conditions					
consistency	%	10			
time	min		30		
temperature	C		30		
concentration					
NaOH	g/L		90	82	
Xylan	g/L			19	
degraded carbohydr.	g/L			2	
PULP					
Yield	%	100			82,8
Viscosity	mL/g	820			880
R18	% odp	87,9			98,5
R10	% odp	91,5			97,6
Xylan	% odp	19,1			5,5

The CCE process is very selective on the removal of xylan. Thus, the cellulose yield is almost not affected and the precipitated and washed xylan contains less than 2% of non-xylose sugars. An overall xylan yield of about 6-7% on odw is estimated assuming a purification yield of 90%. In practice, the CCE filtrate is treated by ultrafiltration to concentrate the xylan in the retentate and to recycle the purified caustic to the CCE treatment (Figure 1).
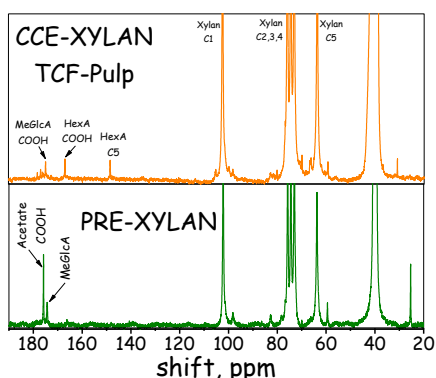
Figure 8: ^{13}C-NMR of xylans isolated from Eucalyptus globulus wood by extraction with 2.5 M NaOH at 90ºC (PRE-XYLAN) and from TCF-bleached Eucalyptus globuluskraft pulp (CCE-Xylan).

The ^{13}C-NMR spectrum of the CCE-Xylan signals the presence ofhexenuronic acid (HexA) in addition to 4O-methylglucuronic acid side chains. The relatively high HexA content of 4.2% (^{1}H-NMR) to 6.7 wt% (^{13}C-NMR) may be attributed to the applied purely alkaline TCF bleaching sequence (O-P-P). Quantitative NMR analyses revealed aglucuronic acid content ranging from4.4 wt% (^{1}H-NMR) to 6.2 wt% (^{13}C-NMR).

Molar mass distributions of the isolated xylans
Beside the purity, molar mass and molar mass distributions constitute important parameters for the evaluation of xylan. They largely depend on the applied isolation techniques. In general, alkali extracted xylan show a higher molar mass and higher purity as compared to xylan extracted by hydrothermal treatments.

Table 2: Macromolecular characterization of xylans isolated from Eucalyptus globulus by different processes and different process steps.

Xylan type	label	P-factor	Mw Da	Mn Da	PDI
Autohydrolysis	VHJ70	200	3 127	1 940	1,6
	VHJ77	135	3 657	1 804	2,0
PRE-XYLAN	FE 279/07		22 971	12 018	1,9
CCE-XYLAN	233/09		15 309	9 120	1,7

The comparative evaluation reveals a clear advantage in molar mass for the alkaline extracted xylans compared to the hydrothermally leached xylans (Table 2, Figure 9).The molar mass of the latter is surprisingly low despite the low prehydrolysis intensity which leads to a very low yield of less than 3 wt% on odw. On the other side the autohydrolysisxylan is water soluble due to the presenceof acetyl groups (28 mol% determined by ^{13}C-NMR).
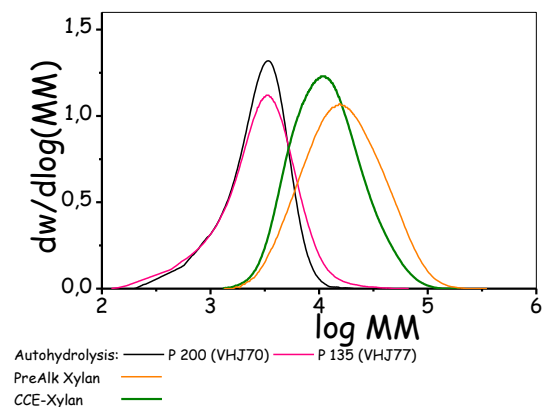

Figure 9: Molar mass distributions (MMDs) of four different purified xylans isolated by hydrothermal treatment (P200, P135), pre-alkaline extraction and cold caustic extraction from Eucalyptus globulus.

Conclusions

In this study, three different processes prior and subsequent to alkaline cooking of *Eucalyptus globulus* were investigated with regard to their efficiency and selectivity of xylan recovery. The following conclusions can be drawn from this study:

- The hydrothermal treatment of *Eucalyptus globulus* allows the removal of polymeric and oligomericxylan in a maximum yield of about 12-13% on odw. In agreement with birch autohydrolysis the maximum carbohydrate yield is achieved at a log (P-X_F) of about 3 corresponding to a treatment at 170ºC for 100 min.For the calculation of the effective xylan recovery the amount of xylan entrapped in the wood void system has to be considered.

- In summary, the hydrolysate from low- to medium intensity autohydrolysisconstitutes an interesting source of xylo-oligosaccharides and polymeric xylan of low molecular weight.

- The recovery of monomeric sugars, primarily xylose, requires the addition of a strong to medium-strong acid to favour the catalytic cleavage of the glycosidic bonds in the released oligo-saccharides rather than the dehydration reactions to furfural. Sulphuric acid is an appropriate catalyst to achieve quantitative hydrolysis to monomeric xylose when applying an intensity of 1.7, expressed as [log(R_0)-pH].The catalytic effect of oxalic acid seems to be comparable to that of sulphuric acid. However, owing to highly scattered results a final conclusioncannot yet be drawn.

- The xylan with the highest molar mass (~23 kDa) can be isolated by alkaline extraction of the wood directly. High alkalinity (*e.g.* 2.5 M NaOH), moderate temperatures (*e.g.* 90ºC) and the absence of a strong nucleophile ensure the isolation of xylan in relevant amounts (~ 6 % on odw) and rather low contamination with lignin. The extracted xylan may be concentrated by multi-step pressure-driven membrane filtration. In case of paper grade production the retentate could be utilized as alkali source for oxygen delignification. In this way most part of the xylan re-precipitates onto the pulp fiber surface which may contribute to an overall yield increase of 3-4% as compared to the standard paper-grade pulp.

- Polymeric xylan of slightly lower molecular weight in similar amounts, 6-7% on odw, can be recovered by cold caustic extraction of a hardwood paper-grade pulp. The alkaline extraction may be accomplished in any step after cooking or bleaching.This treatment allowsthe manufacture of a novel generation of dissolving pulps which seems to be particularly suited for the conversion to Lyocell-type of regenerated cellulosic products[2].

- The combined alkaline pre- and postextractionsleads to the isolation of up to 12% of polymeric xylan on odw. The resulting narrowly distributed, hemi-lean pulp is suited as dissolving pulp, primarily for Lyocell applications.

- The experimental results confirm that the xylan yield can be improved by the implementation of separate extraction steps prior or subsequent to alkaline delignification processes. Both acidic and alkaline treatments support the parallel production of hemicellulose-lean dissolving pulps.

- The evaluation of the economic feasibility requires further extensive experimental studies and process simulation work to answer the many open questions such as the chemical charges, energy requirements, the investments for the additional equipment and the yield and quality of the resulting (dissolving) pulp to name a few.

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