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Prehydrolysis Sulfite Revisited

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Summary: The prehydrolysis of beech wood in water at different temperatures and the impact of this treatment on further pulping stages were explored. Both, increased condensation degree and an increased number of free phenolic hydroxyl groups were found in the lignin isolated after prehydrolysis. An intermediate alkaline extraction (using either NaOH or MgO as base) following the prehydrolysis was explored. Finally, acid sulfite cooks of the differently pre-treated materials were performed, and the obtained materials thoroughly analyzed.

Keywords: biomaterials; degradation; fibers; high performance liquid chromatography (HPLC); polysaccharides

Introduction

Multistage cooking enables more selective pulping processes than one stage cooking. It facilitates the cheap production of high quality pulp and is necessary to achieve a good separation of the different wood components. The alkaline prehydrolysis Kraft process is well established. During aqueous prehydrolysis acetic acid is liberated and in the resulting acid environment a large fraction of the hemicelluloses may be dissolved. Attempts to develop a similar prehydrolysis sulfite process have been undertaken in the past.[1-6] In these experiments reduced susceptibility of the wood in relation to subsequent sulfite pulping was an obstacle that could only be partially overcome by choosing rather impracticable conditions (buffered solutions combined with low temperatures) during the prehydrolysis.[4,5] Several explanations for the observed behavior have been put forward by these early investigators, some of these hypotheses (like a physical agglomeration of small lignin particles during the prehydrolysis)[2] are no longer consistent with today's understanding of wood structure. A sound scientific description of the processes responsible for the observed failures is still missing. Our results should help to establish a basic knowledge for further developments in this area.

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Experimental

Chemicals. Fine chemicals were purchased from Sigma-Aldrich or Merck, SO_2 (l), 99.99 %, was supplied by Linde. Fully deionised water was used for all experiments.

Wood chips. Freshly cut beech wood (*Fagus sylvatica* L.) was ground in frozen condition and fractionated with a Retsch mesh. The residue of the widest-meshed sieve (3.55 mm) was used for the experiments.

Pulping. The experiments were carried out in a lab-scale Parr reactor station with a reactor volume of 450 ml. The steel reactors had each a stirrer, a temperature sensor, and a heating mantle. The indicated starting material (30 g dry matter) was placed in the reactor together with enough water to achieve a total liquid-to-wood ratio of 10:1 (including wood moisture). A process control system was used to perform different pulping stages (prehydrolysis, extraction, or acid magnesium bisulfite pulping). The reactions were stopped by rapid external cooling with ice. The solid residues were filtered off and washed with water. The residues were stored in wet condition in sealed plastic bags for further processing.

Prehydrolysis: Chips were submitted to water-prehydrolysis in the sealed reactor at the conditions indicated in the text. For the calculation of the P-factor from the recorded temperature / time data an activation energy (Ea) of 125.6 kJ/mol was used.[7] To produce sufficient amounts of prehydrolysis residue for subsequent processing, selected prehydrolysis experiments were done in a 10 l digester with forced circulation. In each of those trials 800 g wood (dry mater) was processed; all other conditions were as described above. Alkaline extraction: Extractions were done in the reactor system applying either aqueous MgO (0.13 mol/l, 160 °C, 120 min) or aqueous NaOH (0.5 mol/l, 120 °C, 30 min) as base. Immediately after these experiments a "mud-phase" was separated from the liquor. Acid sulfite cooking: A modern variation of acid magnesium sulfite cooking, including addition of liquid SO_2, was applied with the following parameters: 0.75 mol/l total SO_2, 42 % free SO_2, 148 °C cooking temperature. The process was controlled by the automated process control system to achieve an H-factor of 200. For the H-factor calculation an activation energy (Ea) for delignification of 110 kJ/mol was used. The solid phase obtained in the sulfite cooking stage was sorted into a "pulp" and a "shives" fraction by suspending the residue in 300 ml water (rapid stirring) and passing the suspension through a sieve (mesh aperture 1 mm) with the help of approximately 50 l water from a water hose. The shives fraction remaining in the sieve was analyzed separately, whenever sufficient material was obtained.

Analytical Methods. Kappa numbers were determined according to TAPPI test method T236 cm-85, carbohydrate composition by total hydrolysis and HPLC separation with pulsed amperometric detection (PAD). Dry matter contents were determined by drying in a vacuum oven at 105 °C. Cited lignin contents for solid substrates always comprise Klason lignin and acid soluble lignin (according to TAPPI test method T222 om-98). Lignin contents of liquid phases were calculated from UV/Vis spectra recorded at pH 4.5. An absorption coefficient of 110 l/(g*cm) at 205 nm for dissolved lignin (Tappi-UM-250) and of 35 l/(g*cm) at 233 nm for dissolved lignosulfonates (Lignin Institute test method T-500) was used. Milled wood lignin (MWL) was isolated by standard procedures according to the Björkman method.[8] Permanganate oxidation of MWL samples was carried out according to the method described by Gellerstedt.[9] Acetylation of MWL for subsequent NMR analysis was done as described by Lundquist.[10]

Results

In a previous work[11] a detailed xylan removal kinetic during the aqueous prehydrolysis of beech wood was established. Based on this work, a series of experiments varying both temperature and time of prehydrolysis was carried out. In these experiments the P-factor concept, developed by Lin and Kerr,[12,13] proofed to be a suitable tool for the description of our experiments, i. e. identical P-factors achieved at different temperatures corresponded to very similar residual xylan contents, see Figure 1.

For further experiments a target P-factor of 348 was chosen. At this level of prehydrolysis intensity nearly half of the xylan initially present in the wood was removed, whereas only minor amounts of glucan were dissolved. This P-factor corresponded to a prehydrolysis time of 15 min, 30 min, and 400 min at 190 °C, 170 °C, and 140 °C, respectively.

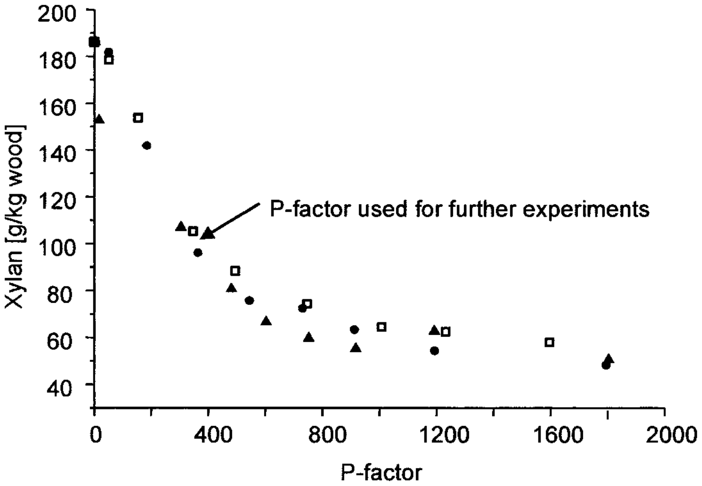

Figure 1. Xylan loss kinetics of beech wood during aqueous prehydrolysis; □ T = 140 °C, ● T = 155 °C, ▲ T = 170 °C.

The following nomenclature will be used in this work:

P......prehydrolysis

E.....alkaline extraction

S.....acid magnesium bisulfite cooking

In our experiments three different sequences for pulping were compared:

I acid magnesium bisulfite cooking of untreated wood (S)

II prehydrolysis - acid magnesium bisulfite cooking (P-S)

III prehydrolysis - alkaline extraction - acid magnesium bisulfite cooking (P-E-S)

These experiments were carried out at three different temperatures during prehydrolysis (140 °C, 170 °C, and 190 °C, respectively) and two different bases during alkaline extraction (NaOH and MgO). Sulfite pulping was always done with the same conditions (see above) that were chosen to match the requirements of our reactor station and to achieve a low Kappa value. No other specific targets were envisaged and the results might deviate significantly from cooking in technical digesters (with a far lower liquid to wood ratio). Table 1 summarizes the principal results of the pulping experiments. In our experiments we observed that the amount of shives or reject depended strongly on the intensity of the fractionating treatment. We tried to standardize this procedure as far as possible to obtain better comparability. Nonetheless, the “shives” fraction mentioned in Table 1 should not be confused with “shives” obtained in a technological process. Probably, a considerable amount of the material indicated here as “shives” would be mechanically broken up and collected with the “pulp” fraction in a technological process. In some of our experiments considerable amounts of “shives” were obtained. Kappa numbers only describe the “pulp” fractions and are therefore no adequate parameter for delignification in these processes. Therefore, and to quantify also the other wood components correctly, the “shives” and “pulp” fractions were analyzed separately for lignin and carbohydrates, whenever enough material was obtained to do so. Then an overall lignin and carbohydrate content for the total solid phase (“pulp” + “shives”) was calculated. These values were used in this work. The chemical composition of the shives fraction was quite similar to the corresponding pulp fraction, with an only slightly higher lignin content. When insignificant amounts of shives were obtained, the compositions of both fractions were assumed to be identical in this calculation. The percentages describing the composition of any solid residue (e.g. prehydrolyzed wood) are marked “% res.” in the following tables. To allow better comparison these values were also converted to percent of initial wood material (% wood).

Table 1. Result of acid magnesium bisulfite cooking experiments from pre-treated materials.

sequence	T (pre-hydrolysis)	total yield	Kappa	shives	xylan		glucan		lignin	
	°C	%		%	%		%		%	
		wood		res.	res.	wood	res.	wood	res.	wood
S	-	52	7.1	1	9.0	4.7	87	45	1.0	0.5
P - S	140	50	52	11	8.9	4.5	81	41	8.4	4.2
	170	47	34	1	8.3	3.9	81	38	4.9	2.3
	190	47	27	1	8.1	3.8	88	41	1.5	0.7
P-E_{NaOH}-S	140	47	57	70	6.3	2.9	77	36	12	5.6
	170	45	48	18	5.8	2.6	83	37	8.7	3.9
P-E_{MgO}-S	140	54	88	66	7.7	4.1	71	37	14	7.4
	170	51	63	62	7.7	3.9	76	39	12	6.1

Lignin, xylan, and glucan composition of final total solid phases (“pulp” +”shives”) cited as % in solid residue (% res.) and calculated on initial wood components (% wood).

Samples of all intermediate stages, as well as the wood itself, were analyzed for carbohydrate composition and lignin content, see Table 2.

The liquid phases from all pulping stages were analyzed likewise for carbohydrate composition, subsequently subjected to total hydrolysis, and again analyzed for carbohydrate composition. Thus, it was possible to distinguish between monomeric and oligomeric carbohydrates. This information is especially important for possible xylan utilization. Therefore the xylan (oligomer) and xylose contents of the liquid phases are stated separately throughout this work.

Table 2. Composition of wood and intermediate solid phases.

stage	T (prehydrolysis)	yield	xylan		glucan		lignin	
	°C	%	%		%		%	
		wood	res.	wood	res.	wood	res.	wood
wood	-	100	17		40		25	
P	140	76	12	8.9	51	39	26	19
	170	75	11	8.4	52	39	25	19
	190	75	12	8.9	54	41	n.d.	
P-E_{NaOH}	140	54	6.8	3.7	66	36	22	12
	170	57	6.9	3.9	66	38	22	12
P-E_{MgO}	140	68	9.3	6.3	57	38	26	18
	170	67	8.8	5.9	59	40	24	16

n.d.: no data

Lignin, xylan, and glucan composition cited as % in solid residue (% res.) and calculated on initial wood components (% wood).

Glucan content is always stated as total glucan, including glucose as well as oligomeric glucan. The lignin content of liquid phases was estimated via UV/Vis spectroscopy. Selected liquors were additionally analyzed for xylonic acid. Because the obtained concentration data depended on dilution factors, this data is only given as % of initial wood substance.

Using this data to trace the fate of the individual wood components throughout the process involves several potential pitfalls: The glucan content of the initial wood is usually underestimated by all analytical techniques. The material removed during a certain stage may not completely be included in the liquid phase associated with the process. Further complications are degradation reactions, e.g. from xylose to xylonic acid or condensation to furfural.

Table 3. Analysis of liquid phases generated in the last stage of the indicated sequence; compounds quantified as % of initial wood material.

liquor from stage	T (prehydrolysis)	xylose (monomer)	xylan (oligomer)	xylonic acid	glucan	lignin
	°C	% wood	% wood	% wood	% wood	% wood
P	140	0.8	8.9	1.4	0.6	2.9
	170	0.3	9.0	0.6	0.7	3.8
	190	0.3	7.6	n.d.	0.4	n.d.
P-E_{NaOH}	140	<0.1	0.5	n.d.	<0.1	11.1
	170	<0.1	0.6	0.3	<0.1	5.5
P-E_{MgO}	140	<0.1	0.7	n.d.	<0.1	1.7
	170	<0.1	0.7	n.d.	<0.1	1.4
S	--	6.0	0.6	4.4	0.5	30.1
P-S	140	0.8	0.8	n.d.	0.1	13.9
	170	1.1	0.4	2.0	0.1	15.7
	190	1.1	0.4	n.d.	0.1	n.d.
P-E_{NaOH}-S	140	0.3	0.1	n.d.	0.1	6.9
	170	0.2	0.1	0.4	0.1	7.9
P-E_{MgO}-S	140	0.6	0.2	n.d.	0.1	10.4
	170	0.6	0.1	n.d.	0.1	10.9

n.d.: no data

Lignin, rendered soluble, is inherently difficult to assess quantitatively. To evaluate the plausibility of the results, the components removed during each stage were quantified in two ways: Using data from Tables 1-3, the difference between the contents observed in the two solid phases associated with the stage (starting material and product) was compared to the amount of wood components actually detected in the liquor generated in the described stage. Considering the multitude of potential side reactions and products this is of course a rather crude approach. Good correlation between both methods was obtained for xylan and lignin results from prehydrolysis and sulfite cooking stages. However, this good correlation was not observed for glucan. For the alkaline extractions, a fairly good agreement was found for lignin but only a small fraction of the xylan removed from the wood was found in the liquor as xylan or its degradation products, e.g. by extraction with NaOH after prehydrolysis at 170 °C the removed xylan amounted to 4.4 % of initial wood material but only 0.9 % of initial wood material was found in the liquor as xylan, xylose, or xylonic acid. In these stages the formation of a slurry from the liquor immediately after the reaction had been observed, also a considerable part of the dissolved carbohydrates might have been decomposed in the alkaline medium.

To elucidate the changes in lignin structure during the different pulping stages we performed additional prehydrolysis and extraction experiments and isolated MWL from the obtained solid residues. The obtained MWL was subjected to standard lignin analyses. The most significant results from these experiments were the so called "condensation degree" from potassium permanganate oxidation (the ratio of degradation products from condensed structures to those from uncondensed lignin structures)[9] and the determination of free phenolic hydroxyl groups by acetylation and ^{1}H-NMR, see Table 4.

Table 4. Results of MWL analysis.

stage	T (prehydrolysis) °C	condensation degree mol %	phenolic OH per 100 C9 units
wood	--	14	15
P	140	18	25
	170	19	26
P-E_{MgO}	140	18	29
	170	19	29
P-E_{NaOH}	140	20	22
	170	20	27

Discussion

Impact of Prehydrolysis

As expected, prehydrolysis hindered delignification in subsequent sulfite pulping stages. Under all studied conditions Kappa values and total lignin content after the sulfite cooking increased compared to single stage sulfite pulping. Possible reactions during the prehydrolysis could involve

a) condensation of lignin molecules,
b) cleavage of lignin bonds,
c) chemical modifications of lignin without condensation or cleavage reactions,
d) changes in the lignin-carbohydrate framework on the covalent as well as on the supramolecular level.
e) reactions with carbohydrate degradation intermediates, e.g. furfural

Any hypothesis to explain the observed lignin deactivation has to take into account that prehydrolysis does not prevent subsequent alkaline Kraft pulping, as long as a certain intensity of prehydrolysis is not exceeded. In our experiments, quite large amounts of lignin were removed during prehydrolysis – a further argument against too simplified explanations.

Our results from MWL isolated from prehydrolysed wood showed that in comparison to MWL from untreated wood both condensation degree and the number of free phenolic hydroxyl groups were increased. Therefore, the analyses of the prehydrolysis residues seems to support the mechanism suggested by Lora:[14] During prehydrolysis two reactions take place: Fragmentation of lignin bonds, hence the increase in free phenolic hydroxyl groups and simultaneous or subsequent re-condensation to form larger units, hence the higher condensation degree. Nonetheless, the particular sensitivity of the acid sulfite process towards prehydrolysis could derive from changes at the possible reaction sites for sulfonation rather than from overall lignin condensation. Experiments with model compounds could help to evaluate this possibility.

For all MWL derived results, not only the exploratory character of these experiments must be considered, but also the significance of MWL isolation for this particular problem might be questioned. Only a small part of the lignin present in wood is found in MWL and it might well be that the lignin most severely altered by a certain treatment, and hence the most interesting, is not retained during MWL isolation.

Influence of Prehydrolysis-Temperature

After early investigators of a possible prehydrolysis sulfite process discovered that prehydrolysis deactivated lignin related to acid sulfite cooking, it was tried to use milder prehydrolysis conditions by performing the prehydrolysis at lower temperatures.[1,3-5] Not surprisingly, when wood was subjected to prehydrolysis at different temperatures for similar times better cooking results were obtained at lower temperatures. However, also the benefits, e.g. xylan removal, decrease strongly with decreasing temperature. With the data from most of the existing studies it is difficult to compare different prehydrolysis strategies because the intensity of the studied prehydrolyses vary considerably. We decided to follow a different approach by studying prehydrolysis at a constant level of intensity. To this end we used the P-factor concept that integrates time and temperature into one variable. From this approach a totally different view emerged. For all studied pulping sequences lower Kappa numbers, lower lignin contents, and lower shives contents were achieved at higher temperatures (i.e. shorter prehydrolysis times), see Table 1 and Figure 2.

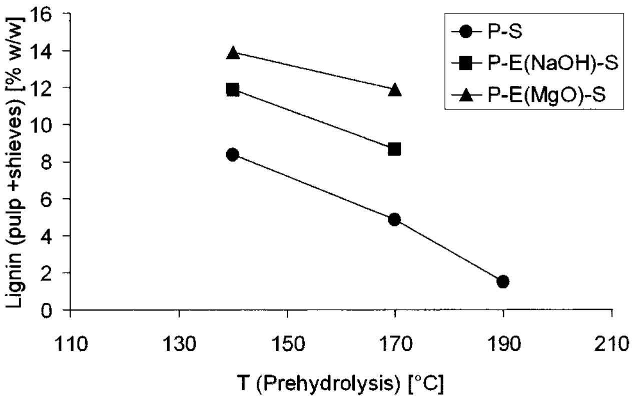

Figure 2. Influence of prehydrolysis temperature on delignification in 2-stage (P-S) and 3-stage (P-E_{NaOH}-S and P-E_{MgO}-S) acid sulfite cooking.

At least in the studied temperature range from 140 °C to 190 °C, high temperatures for a short period of time cause less lignin deactivation than low temperatures applied for a long time. Prehydrolysis at very low temperatures (e.g. 105 °C)[4] was not included in this comparison. Even if our desired amount of xylan removal could be achieved at this temperature, prehydrolysis would take impractical lengths of time.

Effects of Alkaline Extraction

To remove reactive lignin fragments generated during prehydrolysis, an intermediate extraction stage was included between prehydrolysis and acid sulfite cooking. Facilitation of alkaline lignin extraction by previous prehydrolysis was described e.g. by Lora[14,15] and Overbeck.[6] Contrary to our initial expectations, the pulps derived from the subsequent acid sulfite cooking were less delignified than those obtained from the prehydrolysate without intermediate extraction. In Table 1 it can be clearly seen that the overall pulping efficiency decreased in the order S > P-S > P-E_{NaOH}-S > P-E_{MgO}-S.

Obviously, alkaline extraction (at least at the chosen conditions) deactivated lignin specifically regarding to subsequent acid sulfite pulping. This negative impact overcompensated any positive effects from the lignin extraction that was per se successful, as may be seen from the fact that a quarter of the initial wood lignin was removed during alkaline extraction with NaOH following prehydrolysis at 170 °C (data from Table 2).

The reason for this behavior is yet open to speculation. Our MWL analysis showed no significant differences in condensation degree or free phenolic hydroxyl content before and after alkaline extraction. Most probable, alkaline treatment at the given conditions destroys those moieties in the lignin structure necessary for a successful sulfite pulping process. It should be mentioned that our experimental setup (about 100 ml air in the pressure vessels, removing the intermediates from the vessel and hence saturating them with air) might favor oxidation reactions. Oxidation reactions of lignins or lignin model compounds under alkaline conditions are well known[16-18] and are the basis for a commercial production of vanillin from softwood spent liquor.

The Removed Wood Components

More than half of the initial xylan was removed in the prehydrolysis steps. About 90 % of the dissolved xylan was present in oligomeric form. Therefore, possible applications of the prehydrolysis liquor would have to be either based on oligomers or include a "post-hydrolytic step" to degrade the xylan oligomers to xylose monomers. Although the aim of the initial prehydrolysis was the removal of xylan (hemicelluloses), still a fair amount of lignin (6% of wood substance, about a quarter of the lignin initially present in the wood) was removed during prehydrolysis. This constitutes a problem for possible commercial utilization of the xylan removed during prehydrolysis. Figure 3 illustrates the ratio of the analyzed (UV/Vis and HPLC) compounds in the liquor. There is no correction for "unknowns" or "others" (like minor sugars) in this figure but, as mentioned above, the agreement between quantities found in the liquor and material removed from the solid phase is quite good for this stage. Only minor amounts of the xylan removed in the alkaline extraction steps were found in the analyzed liquor.

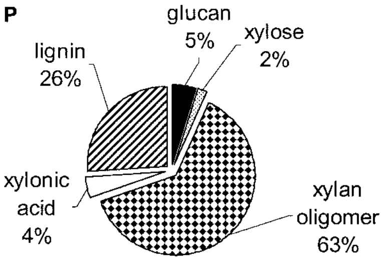

Figure 3. Ratio of lignin, xylan, and its degradation products in the liquor obtained from prehydrolysis at 170 °C.

The missing xylan might either have been precipitated in the "mud" phase or degraded in the alkaline medium. Accordingly, the analyzed liquors from these stages contained mainly lignin but can not be considered representative samples.

In the final acid bisulfite cooking steps the amount of removed xylan depended strongly on the used sequence: Although about 15 % of wood substance were removed as xylan in the single step acid bisulfite cooking process from untreated wood, only 4.5 % of wood substance were removed in the sulfite step of the P-S sequence. The total amount of lignin removed was similarly reduced, therefore the relative composition of the sulfite liquor from the P-S sequence is quite similar to the composition of the one stage sulfite cooking liquor, see Figure 4. The relative lignin content is slightly increased and the xylose to xylonic acid ratio is shifted to the latter.

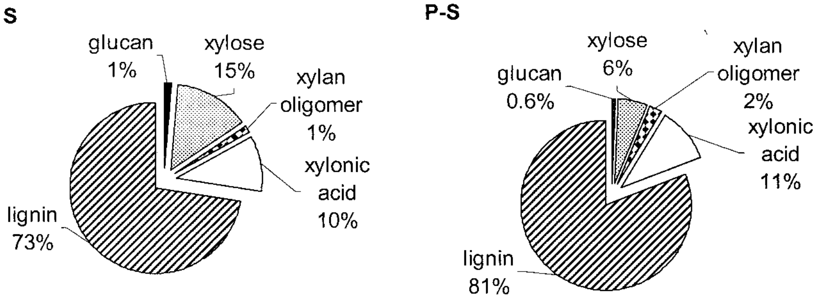

Figure 4. Ratio of lignin, xylan, and its degradation products in sulfite cooking liquors from one stage (above) and two stage (right) sulfite cooking. The used pulping sequences are indicated above each diagram. Prehydrolysis (for P-S) was done at 170 °C.

In the P-E_{NaOH}-S sequence the bulk of the remaining xylan and again significant amounts of lignin were removed during the alkaline extraction, therefore only slightly more than 1 % wood substance was removed as xylan in the final sulfite stage. Lignin accounted for nearly 90 % of the analyzed compounds in this liquor. Therefore by a three stage pulping process the nearly quantitative separation of the by-products from the sulfite liquor was achieved.

Large losses of glucan were not observed in any of the studied pulping stages.

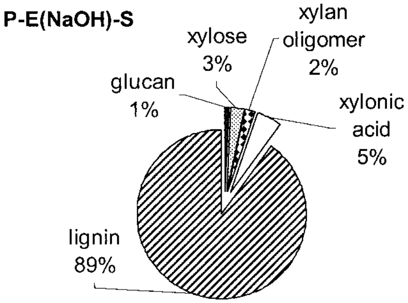

Figure 5. Ratio of lignin, xylan, and its degradation products in sulfite cooking liquor from three stage sulfite cooking. A P-E_{NaOH}-S pulping sequence with prehydrolysis at 170 °C was applied.

Conclusions

The deactivation of lignin in relation to sulfite pulping by aqueous prehydrolysis involves both rupture of lignin bonds and lignin condensation. Pulping sequences involving prehydrolysis at high temperatures for a short time yielded better overall cooking results than sequences achieving the same intensity of prehydrolysis by applying lower temperatures for longer times. Alkaline extraction following prehydrolysis, though removing considerable amounts of lignin, deactivated the wood further in relation to delignification in subsequent acid sulfite pulping.

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[1] A. J. Corey, O. Maass, *Can. J. Research* **1935**, *13B*, 289-295.
[2] A. J. Corey, O. Maass, *Can. J. Research* **1935**, *13*, 149-155.
[3] A. J. Corey, J. M. Calhoun, O. Maass, *Can. J. Research* **1937**, *15*, 168-185.
[4] W. Lautsch, *Holz* **1942**, *5/6*, 119-127.
[5] W. Lautsch, *Holz* **1943**, *6*, 148-151.
[6] W. Overbeck, H. Muler, *Berichte* **1942**, *75*, 547.
[7] H. Sixta Habilitation Thesis, Graz University of Technology 1995.
[8] A. Bjökman, *Svensk Papperstidning* **1956**, *59*, 477-485.
[9] G. Gellerstedt in *Methods in Lignin Chemistry*, Eds. Lin, S. Y. and Dence, C. W., Springer, Berlin, 1992, pp 322-333.
[10] K. Lundquist in *Methods in Lignin Chemistry*, Eds. Lin, S. Y. and Dence, C. W., Springer, Berlin, 1992, pp 242-249.
[11] H. Sixta, G. Schild, T. Baldinger, *Das Papier* **1992**, 527-539.
[12] C. K. Lin, PhD, North carolina State University, 1979.
[13] A. J. Kerr, V. D. Harwood, *Appita* **1976**, *30*, 135-142.
[14] J. H. Lora, M. Wayman, *Tappi* **1978**, *61*, 47-50.
[15] J. H. Lora, M. Wayman, *Tappi* **1978**, *61*, 88-89.
[16] K. Kratzl, P. Claus, W. Lonsky, J. S. Gratzl, *Wood Science and Technology* **1974**, *8*, 35-49.
[17] K. Kratzl, J. Gratzl, P. Claus, *Advances in Chemistry Series* **1966**, *59*, 157-176.
[18] M. Holocher-Ertl, P. Fricko, K. Kratzl *Oxygen Oxidation of Lignins*: Stockholm, 1981; Vol. 2, pp 83-89.