FORMATION OF INSOLUBLE COMPONENTS DURING AUTOHYDROLYSIS OF EUCALYPTUS GLOBULUS

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Autohydrolysis reactions of lignin leading to the formation of insoluble components and scaling during water prehydrolysis and during handling of the prehydrolysate were studied. Scaling represents a major problem for the extraction of valuable hemicellulose degradation products from the prehydrolysate. Various lignin fractions isolated from autohydrolysis experiments were extensively characterised. In addition, lignin mass balances were established. During autohydrolysis, lignin is degraded to a significant extent through cleavage of aryl-ether bonds resulting in a considerable reduction of the molecular weight. Some of the dissolved lignin degradation products remain soluble in the prehydrolysate, while degradation products characterised by a higher molecular weight precipitate upon cooling. Exposure of water prehydrolysates to 170°C leads to the formation of highly condensed precipitates characterised by an increased molecular weight. These precipitates, denoted as PT-fraction, form scaling on the reactor wall. Condensation reactions of soluble and insoluble lignin degradation products dissolved in the prehydrolysate were identified as the origin of the PT-fraction.

Keywords: autohydrolysis, lignin degradation, residual lignin, MWL, NMR, prehydrolysis kraft pulping, biorefinery

Introduction

Dissolving pulps are pure cellulose pulps with an extremely low content of hemicelluloses and lignin. In contrast to paper pulps, hemicelluloses have to be removed during the production of dissolving pulps. This results in low pulp yields of 30 to 40 wt-% based on wood, depending on the wood species, the production process and the purity grade of the pulp. The hemicelluloses, which are dissolved together with the lignin in the spent liquors of the production processes, are normally combusted for power generation. However, the approximate calorific value of hemicelluloses of about 14 MJ/kg is low compared to that of about 25 MJ/kg for lignin. Therefore, the hemicelluloses should be used as a source for valuable products. As an example, the dietetic sweetener xylitol is produced on the basis of hardwood hemicelluloses. Also Acetic acid and furfural are products that are formed during acid degradation of hardwood xylan. The Lenzing AG is a representative for the commercial use of hardwood hemicelluloses by selling...
xylose, which is the starting product for xylitol. Acetic acid and furfural are extracted from the spent liquors of dissolving pulp production. [1].

Two different processes are used for the production of dissolving pulps from wood: the prehydrolysis kraft (PHK) process and the acid sulphite process. The acid sulphite process is the dominant process for dissolving pulp production. However, the PHK process has numerous advantages compared to the acid sulphite process, and PHK pulping, particularly of hardwoods, is gaining importance [2, 3]. Nevertheless, recovery of dissolved hemicelluloses is not possible so far. The selective removal of hemicelluloses during the PHK process is achieved through autohydrolysis of the wood chips prior to kraft cooking. During this prehydrolysis step, 15-30 wt-% of the dry matter of hardwoods, depending on the intensity of the treatment, is dissolved. At present, steam prehydrolysis conducted at a low liquor to wood ratio is state of the art. The dissolved material is neutralised with alkaline cooking liquor subsequent to steam prehydrolysis and then displaced from the digester [2, 4]. The neutralisation step results in a complete degradation of the dissolved carbohydrates and the neutralisation liquor is combusted. If a water prehydrolysis conducted at a higher liquor to wood ratio is applied without subsequent neutralisation, the resulting prehydrolysate contains important amounts of xylan degradation products but also substantial amounts of lignin [5-7]. The prehydrolysate could represent a rewarding source of carbohydrates. However, insoluble components precipitating from the prehydrolysate tend to form deposits that pose major difficulties during handling and processing of the hydrolysate [8-11]. Measures to handle the scaling and deposition problems have to be developed to allow for the recovery of the valuable hemicellulose degradation products. Therefore, a better knowledge about the origin and behaviour of the insoluble components contained within the prehydrolysate is required. The most important results of a study investigating the composition of the insoluble components, the reason for their formation and their behaviour are summarized in this paper. The results have previously been published in detail in a series of publications [12-15].

**Experimental**

Autohydrolysis experiments were carried out with extractive-free E. globulus wood chips with a particle size between 2.50 and 3.55 mm in a Parr reactor station equipped with mechanical stirring and a reactor volume of 450 ml. The reaction was carried out at a water to wood ratio of 5:1 and at 170°C. When attaining the desired reaction time, the prehydrolysate was withdrawn in an isothermal phase separation step and transferred into a second reactor. In general, the prehydrolysate and the wood residue were immediately cooled. In one particular experiment, denoted as “temperature treatment” (TT), the prehydrolysate was separated from the wood at a P-factor of 650 and then further treated under prehydrolysis conditions until a total P-factor of 1570 was attained. The black resinous precipitate formed during this particular experiment on the reactor wall was dissolved in acetone/water (5:1) and denoted as PT-fraction.

In each experiment, insoluble lignin degradation products were isolated from the prehydrolysate by centrifugation (I-fraction) and soluble degradation products were extracted with ethylacetate (Et-O-Ac extract) (Figure 1). Lignin from the original wood and from the wood residues after autohydrolysis was isolated as milled wood lignin (MWL). The lignin fractions were characterised by sugar analyses, methoxy group determinations, elemental analyses, SEC, and quantitative NMR-spectroscopy of the acetylated samples.
The experimental setup, the isolation of lignin fractions and the analytical procedures are described in detail in [15]. Quantification of lignin for the purpose of mass balances was based on Klason lignin and acid soluble lignin determination as described in [13].

**Figure 1.** Scheme of different fractions obtained from the prehydrolysis experiments.

### Results and Discussion

The insoluble components (I-fraction) contained within the water prehydrolysate were identified as relatively pure lignin. I-fractions obtained from autohydrolysis experiments conducted at 170°C and at a P-factor of 600 showed FTIR spectra that were almost identical to those of lignin isolated from native *E. globulus* wood. Qualitative characterisation using 2D NMR HSQC spectroscopy revealed that the I-fraction contained all structural features typical for native lignin. In addition, some other structural features were found, which were not present in the native lignin that was used as a reference [12]. Subsequently a detailed study of the reactions of lignin under autohydrolysis conditions typical for the PHK process in order to identify the reasons for the formation of insoluble components during water prehydrolysis. All lignin containing fractions formed during water prehydrolysis were isolated and characterised in order to fully understand the reactions occurring during the autohydrolysis:

Lignin contained in the wood residue was isolated as MWL, soluble lignin was extracted with EtOAc from the hydrolysate and the I-fraction was isolated by centrifugation. MWL was isolated from the native *E. globulus* wood as the reference lignin. These four lignin fractions were then investigated in detail.

**Characterisation of Lignin Fractions**

Native lignin. MWL was isolated from the native wood yielding 46 wt-% based on the Klason lignin content. Comparison of analysis results of this MWL with recent literature data on eucalypt lignins revealed significant differences. The content of methoxy groups and of β-O-4 bonds was 140 and 35 per 100 phenylpropane units, respectively [14, 15]. These values were clearly lower than the literature values for eucalypt lignins published by Capanema et al. [16] and Evtuguin et al. [17]. Presumably, differences in the extraction procedure of the wood prior to lignin isolation were responsible for the discrepancy between these values. In the papers cited, wood was extracted with boiling 0.3 wt-% NaOH to remove tannins. During this treatment, a portion of lignin rich in guaiacyl and hydroxyphenylpropane units is also removed [18]. For the present investigation, only a mild extraction with acetone/water (9:1) was performed. We tried to avoid changes of the lignin structure and its reactivity so that we could draw clear conclusions concerning the autohydrolysis process. The differences between our values and those reported in the literature may also be explained by the presence of residual amounts of polyphenolic impurities and an alkali-soluble lignin fraction rich in guaiacyl and hydroxyphenylpropane units in MWL isolated from sources not subjected to
alkaline pre-extraction. However, the amounts of primary and secondary aliphatic hydroxyl groups and phenolic hydroxyl groups found in the native MWL are in agreement with values published for E. grandis MWL (Capanema et al. 2005).

Prehydrolysed lignin fractions. FTIR spectra of all lignin fractions isolated from the same water prehydrolysis experiment conducted at P-factor 670 showed the typical lignin bands in the fingerprint region. A yield of 1.4 wt-% (based on wood) of the I-fraction was obtained and 1.3 wt-% (based on wood) of the EtOAc extract. The amount of the EtOAc extract corresponded well to the concentration of soluble lignin in the prehydrolysate as determined by UV/Vis spectrometry. It was concluded that the extraction was efficient. Comparison of the FTIR spectra of the prehydrolysed lignin fractions to the spectrum of native lignin revealed that prehydrolysis initiated changes in all lignin fractions. All prehydrolysed lignin fractions exhibited a higher carbon content and lower oxygen and hydrogen contents compared to native lignin. This was attributed to condensation reactions and to the elimination of hydroxyl groups. Quantitative NMR spectra confirmed an increased degree of condensation of the aromatic ring and a reduced content of aliphatic hydroxyl groups in all prehydrolysed lignin fractions. All prehydrolysed lignin fractions had an increased content of phenolic hydroxyl groups, indicating the occurrence of cleavage reactions of the aryl-ether bonds of lignin during prehydrolysis. In addition, all fractions showed a reduced content of β-O-4 bonds, compared to native lignin. The cleavage reactions resulted in a molecular weight reduction of all fractions compared to native lignin. SEC revealed a slight but significant reduction in molecular weight of the lignin from the residual wood. The EtOAc extract was composed of low molecular weight lignin degradation products, containing substantial amounts of monomers. The I-fraction comprised components with a molecular weight between MWL and EtOAc extract. The SEC chromatogram of I showed strong overlapping with both, MWL and EtOAc extract (Figure 2).

The results of SEC were in agreement with the content of β-O-4 bonds and phenolic hydroxyl groups in the lignin fractions. The low molecular weight EtOAc extract showed the lowest content of β-O-4 bonds and the highest one in phenolic hydroxyl groups. The I-fraction contained intermediate amounts of β-O-4 and phenolic hydroxyl moieties, while the MWL isolated from the wood residue had the highest content of β-O-4 bonds and the lowest one of phenolic hydroxyl groups. Thus, although an increased degree of condensation was found in all prehydrolysed lignin fractions by NMR, prehydrolysis resulted in a reduced molecular weight of all fractions compared to native lignin. It was concluded that degradation reactions prevailed over condensation reactions at P-factor 670. The chemical structure of condensation products could not be identified using NMR spectroscopy. Condensation of Cα of
the phenylpropane side chain with the aromatic ring resulting in diphenylmethane structures is often assumed to occur under acidic conditions [19, 20]. However, no diphenylmethane structures could be detected in any of the investigated lignin fractions.

The FTIR spectrum of the EtOAc extract indicated a high content of carbonyl groups. Using NMR spectroscopy, syringaldehyde and sinapaldehyde were detected as the major products in this fraction, which was otherwise a complex mixture of various lignin degradation products. Syringaldehyde and sinapaldehyde are reaction products, which are typical for a homolytic reaction mechanism during cleavage of β-O-4 bonds [21]. In the EtOAc extract and in the I-fraction, an increased amount of β-β (resinol) structures was detected. Resinol structures are typical reaction products of radical coupling reactions of reaction intermediates which are formed during the homolytic cleavage of β-O-4 bonds. Based on the presence of these typical reaction products, it was concluded that homolytic cleavage of β-O-4 bonds occurs during water prehydrolysis.

In conclusion the lignin underwent extensive degradation reactions and structural changes during water prehydrolysis at a P-factor of 670 [15]. Lignin degradation products were dissolved in the prehydrolysate only in small amounts due to their limited solubility in the acidic aqueous medium. Low molecular weight products remained in solution, while products with a higher molecular weight precipitated upon cooling, forming the I-fraction. The main reaction of lignin during water prehydrolysis was the homolytic cleavage of aryl-ether bonds. Condensation reactions also occurred, but the cleavage reactions prevailed.

Influence of Autohydrolysis Intensity on the Chemical Structure of Lignin Fractions

The intensity of autohydrolytic treatments strongly influences the reactions of lignin. Fast cleavage reactions prevail in the beginning of the reaction, whereas, slower condensation reactions result in a molecular weight increase at increasing autohydrolysis intensities [22]. These consecutive reactions lead to an optimum autohydrolysis intensity with maximum lignin removal in subsequent pulping stages. This optimum was attained at a P-factor of approximately 700 during PHK pulping of *E. urograndis* [23]. The changes in the lignin composition and functionality at prehydrolysis intensities higher and lower than this optimum were also examined for the following reasons:

- It should be clarified if carbohydrate degradation products contribute to the condensation reactions.
- It has been published that scaling problems increase under extensive prehydrolysis conditions.
- It was unclear if the lignin degradation products dissolved in the hydrolysate undergo condensation reactions resulting in an increased molecular weight.
- No quantitative information on the extent of lignin degradation and on the chemical structure of lignin degradation products formed during water prehydrolysis has been published yet.

Therefore, lignin fractions were isolated from water prehydrolysis experiments at P-factors of 320, 670 and 1540 and compared to each other [14]. The most important findings are:

The content of carbohydrate impurities in the MWL isolated from the wood residues was reduced with increasing P-factor. This was attributed to the progressive cleavage of the bonds between lignin and carbohydrates. The content of methoxy groups in the MWL fractions was
independent of the P-factor. It was concluded that sugar degradation products did not contribute to the MWL and that no demethoxylation reactions occurred during water prehydrolysis. Quantitative NMR spectroscopy revealed that the substitution pattern of the aromatic ring in the residual lignin changed with increasing prehydrolysis intensity. Protons were replaced and the degree of condensation increased, whereas oxygen substitution did not change to a significant extent. Strong lignin degradation was evident in the decrease in molar amount of β-O-4 bonds. Compared to native lignin, the β-O-4 content halved after treatment at a P-factor of 1540. Primary and secondary hydroxyl groups showed a similar trend and their content was also reduced by 50%. At the same time, the content of phenolic hydroxyl groups doubled. The progress of the most significant structural changes in MWL during prehydrolysis is given in Figure 3.

![Figure 3](image_url)

**Figure 3.** Development of the abundance of selected functional groups in the MWL as a function of the prehydrolysis intensity.

The important decrease in aliphatic hydroxyl groups in residual lignin after autohydrolysis is mainly responsible for the deactivation of the sulphonation reaction in subsequent acid sulphite processes, since these groups represent the reactions sites in lignin for sulphonation. SEC of the MWL fractions showed a slight but significant decrease of the molecular weight with progressing prehydrolysis intensity. Obviously, in the residual lignin isolated from the wood residues as MWL, degradation reactions prevailed over condensation reactions, even at P-factor 1540. The reduced reactivity towards kraft and organic solvent delignification occurring at these high P-factors could not be explained by the structural changes of residual lignin observed in this study. The I-fraction was obtained in a maximum yield at P-factor 670. The slightly reduced yield of I-fraction at P-factor 1540 was attributed to its reprecipitation on the wood surface. The molecular weight distribution of the I-fraction was independent of the prehydrolysis intensity. Even at P-factor 1540, no contribution of furfural condensation products could be detected, since the methoxy group content remained constant. However, the I-fraction was subjected to the same kind of reactions as the residual lignin in the wood: With increasing prehydrolysis intensity, progressive elimination of aliphatic hydroxyl groups and β-O-4 bonds occurred, as well as progressive increase in phenolic hydroxyl groups. Concurrently, the degree of condensation increased considerably. The molecular weight distribution of the I-fraction was only slightly affected by the altering P-factor: A minor reduction in the molecular weight was observed with increasing autohydrolysis intensity. The β-O-4 cleavage reactions observed in the I-fractions should lead to a considerable decrease in molecular weight which is not the case. Thus the condensation reactions must counterbalance the degradation reactions. As will be discussed later, high molecular weight components that are formed by condensation reactions from the I-fraction precipitate on the wood surface. The fact that the molecular weight distribution of the I-fraction does not significantly change, regardless to the changes in its chemical structure, proves that precipitation of the I-fraction during cooling of the hydrolysate is due to its high
molecular weight. The yield of the EtOAc extract increased with increasing P-factor. A decreasing methoxyl group content indicated the progressive incorporation of non-lignin products in this fraction. This could be attributed to increasing contents of HMF. In contrast to furfural, HMF is not removed during vacuum evaporation of the EtOAc extract. The concentration of syringaldehyde increased when the reaction time was extended. Sinapaldehyde and resinol structures had maximum concentrations at P-factor 670.

**Amount and Origin of Dissolved Lignin**

Material balances based on Klason lignin and ASL (acid soluble lignin) determinations should reveal what amount of lignin is dissolved at P-factors of 300, 600 and 1500 during the water prehydrolysis process [13]. The material balances confirmed that the I-fraction was maximum at P-factor 600 and was reduced at a higher P-factor of 1500 (Table 1). The bulk of lignin remained soluble in the prehydrolysate and in the wash filtrate even after centrifugation. With rising P-factor, the amount of ASL in the wood residue (WR) was clearly reduced, while the amount of soluble lignin in the hydrolysate was slightly increased. The amount of ASL, which was removed from the wood, corresponded well to the amount of soluble lignin detected in the hydrolysate. It was concluded that ASL contained in the native wood was progressively dissolved during water prehydrolysis. This portion of lignin remained dissolved after cooling and centrifugation of the hydrolysate.

At P-factors of 300 and 600, Klason lignin dissolved only sparingly - about 5-6 wt-% of the primary lignin content in the wood. This amount corresponded well to the I-fraction. It was concluded that the I-fraction resulted from dissolution of part of the Klason lignin. This is in agreement with the structural features and the polymeric character of the I-fraction, which clearly demonstrate its origin as a degradation product of native lignin.

At P-factor 1500, a slight increase in the amount of Klason lignin in the wood residue was observed. This increase can partly be explained by the reprecipitation of part of the I-fraction on the wood surface. Condensation reactions of dissolved lignin, of sugar degradation products and of polyphenolic extractives might also contribute to this increased Klason lignin value.

The usual removal of extractives prior to the determination of Klason lignin and ASL values given in Table 1, using soxhlet extraction with ethanol and toluene was omitted. The reason is that a substantial part of the lignin contained in the wood residue dissolves in organic solvents after autohydrolysis. Removal of this solvent soluble lignin portion would considerably falsify the results. Consequently soxhlet extraction was also omitted prior to analysis of the native wood to obtain comparable results. The Klason lignin and ASL contents determined after soxhlet extraction are given in parentheses in Table 1 for comparison.

<table>
<thead>
<tr>
<th>P-factor</th>
<th>Klason lignin in wood/WR</th>
<th>ASL in wood/WR</th>
<th>I-fraction</th>
<th>Soluble lignin in hydrolysate + wash filtrate</th>
<th>Total Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>243 (229)*</td>
<td>52 (48)*</td>
<td>-</td>
<td>-</td>
<td>294 (277)*</td>
</tr>
<tr>
<td>300</td>
<td>231</td>
<td>19</td>
<td>11</td>
<td>32</td>
<td>293</td>
</tr>
<tr>
<td>600</td>
<td>230</td>
<td>15</td>
<td>13</td>
<td>35</td>
<td>292</td>
</tr>
<tr>
<td>1500</td>
<td>239</td>
<td>11</td>
<td>11</td>
<td>36</td>
<td>296</td>
</tr>
</tbody>
</table>

All values given in g per kg of the original wood; * Soxhlet extraction prior to analysis
**Formation of Condensed Lignin Precipitates**

The worst scaling problems occur in continuous prehydrolysis digesters [8, 11]. Continuous prehydrolysis results in a permanent contact of the prehydrolysate with the inner surface of the digester. It might be expected that storage of prehydrolysates in tanks at high temperature also leads to the formation of scaling problems. One of the main objectives of this study was to identify the origin of the scaling problems. Scaling occurs on any surface available. It was useful to study the formation of scaling in the absence of wood, because the wood represents an additional surface where scaling can take place. Scaling on the wood surface is difficult to distinguish from the wood itself. Hence, to study scaling formation, prehydrolysates were treated under prehydrolysis conditions in the displacement reactor after the phase separation step.

The resinous precipitates deposited on the reactor wall after temperature treatment of the hydrolysate had a similar chemical structure as the I-fraction and were, hence, identified as another form of lignin degradation products [12]. The resinous precipitates (PT-fraction) were characterised by a drastically increased molecular weight compared to the lignin degradation products isolated from a prehydrolysate without TT. This led to the conclusion that the PT-fraction was a condensation product of lower molecular weight lignin degradation products dissolved in the hydrolysate. The molecular weight distribution was broad and components with a molecular weight similar to the I-fraction were included in the PT-fraction as well as components with a higher molecular weight than the native MWL (Figure 4). The molecular weight distribution of the I-fraction was not affected by the TT. The methoxyl group content of 18.3 % was only slightly lower than that of native lignin.

Thus, contribution of furfural to the formation of PT was considered to be of minor importance. Structural characterisation of PT using NMR spectroscopy posed a problem. Due to the high molecular weight the resolution of the spectra was low. A curved baseline in quantitative $^{13}$C spectra impaired quantification of most lignin moieties. Only the hydroxyl groups could be quantified. Comparison to an I-fraction obtained under similar autohydrolysis conditions revealed similarities [14]. In this case NMR spectroscopy could not assist in elucidating chemical pathways.

Leschinsky et al. [12] studied the formation of resinous precipitates by means of carbon balances by varying the duration of the temperature treatment. It was revealed that prolonged TT led to increasing amounts of PT-fraction. Surprisingly, the amount of I-fraction, which was separated by centrifugation from the hydrolysate subsequent to TT, remained constant over the course of the treatment. Due to the similar chemical structure, it was expected that the PT-fraction is formed by condensation of I-fractions, resulting in a reduced amount of I-fraction. The increasing formation of PT-fraction was reflected by a drop in the

**Figure 4:** SEC chromatograms of the fractions isolated after temperature treatment of prehydrolysates. TT P* denotes the sum of a P-factor of 650 and TT-factor of 920.
carbon content in the soluble part of the hydrolysate and it was concluded that soluble lignin degradation products are transformed into insoluble components.

Conclusions

During autohydrolysis, lignin is degraded to a significant extent through cleavage of aryl-ether bonds resulting in a significant reduction of the molecular weight. As a result of these cleavage reactions, the degraded lignin is characterised by a drastically increased content of phenolic hydroxyl groups and a reduced content of aliphatic hydroxyl groups. Evidence for the occurrence of a homolytic cleavage mechanism was found. Condensation reactions change the substitution pattern of the aromatic ring.

As a result of the degradation reactions, lower molecular weight lignin degradation products are dissolved in relatively small amounts due to their low solubility in the acidic aqueous prehydrolysate. Some of the dissolved lignin degradation products remain soluble in the prehydrolysate, while degradation products characterised by a higher molecular weight precipitate upon cooling.

The dissolved lignin degradation products are highly reactive. At high prehydrolysis intensities and during storage of prehydrolysate at elevated temperatures, condensation of the dissolved lignin leads to the formation of resinous precipitates characterised by an increased molecular weight. Further research is focused on the control of the formation of these high molecular weight lignin deposits and on the purification of prehydrolysates.

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