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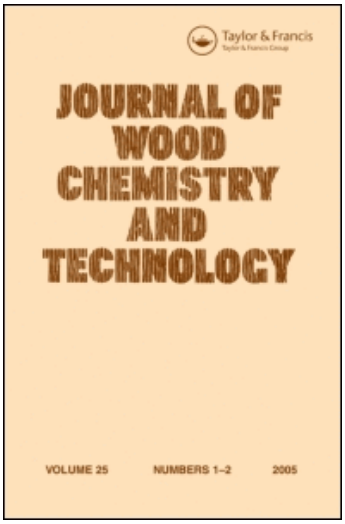

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Characterization of Residual Lignins Isolated from Unbleached and Semibleached Softwood Kraft Pulps

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CHARACTERIZATION OF RESIDUAL LIGNINS ISOLATED FROM UNBLEACHED AND SEMIBLEACHED SOFTWOOD KRAFT PULPS

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Keywords: Kraft pulp, Semibleached kraft pulp, Residual lignins, Lignin-carbohydrate linkages, Cellulolytic enzymes, Cellulolytic enzyme lignins.

ABSTRACT

Residual lignins in an unbleached and a semibleached softwood (Pinus taeda L.) kraft pulp were isolated by enzymatic hydrolysis of polysaccharides in the pulps. After purification, the residual lignins were characterized. A dissolved lignin was also isolated from the alkaline extraction spent liquor by acidification and characterized.

Results of the characterization indicate that extensive degradation of residual lignin in kraft pulp occurred during the first two stages of bleaching. The results also strongly support the previous finding that stable covalent linkages between residual lignins and carbohydrates in pulp may be the most probable cause for the residual lignins to resist delignification during kraft pulping and prebleaching.

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INTRODUCTION

A major drawback of a kraft pulping process is the relatively high residual lignin content of the resulting pulp. This considerable amount of residual lignin cannot be further removed by extended cooking without causing severe degradation of the pulp. The cause(s) for the resistance of the residual lignin to delignification is not well known in spite of appreciable research work done in this field.

One plausible explanation for the encountered resistence is that residual lignins are covalently linked to carbohydrates in pulp. Results of recent investigations on the formation and stability of lignin-carbohydrate covalent bonds seem to support the existence of such covalent bondings in kraft pulps. Upon characterization of residual lignin preparations isolated from a bleachable grade kraft pulp by selective enzymatic hydrolysis of the polysaccharides, Yamasaki et al.[1] found that the residual lignin contained substantial amounts of carbohydrates and was degraded to a less extent than the kraft lignin. They suggested that the cause for its lower extent of reaction and its resistance to delignification during kraft pulping might be attributable to stable lignin-hemicellulose linkages. Benzyl ether linkages between lignin and carbohydrates are well known to form during lignin biosynthesis,[2,3] and the existence of lignin carbohydrate complex (LCC) in wood and isolated lignin has been investigated extensively[4-7]. Yamasaki et al.[1] suggested that non-phenolic α-ether type LCC may be stable under alkali pulping conditions. Using model compound, Taneda et al.[8] recently not only confirmed the stability of non-phenolic LCC under alkali pulping conditions, but also found that the stable α-ether bonds retard the hydrolysis of the adjacent β-ether linkages. The existence of lignin-carbohydrate bonds in unbleached loblolly pine kraft pulp was recently confirmed by Minor[9] in his methylation analysis of the carbohydrates in the residual lignin isolated by the enzymatic procedure similar to that used by Yamasaki, et al.[1]

Lignin carbohydrate linkages may also be formed during pulping. Formation of alkali-stable carbon-carbon bonds between

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lignin and carbohydrate fragments via aldol condensation during alkaline pulping has recently been demonstrated[10]. Formation of stable lignin-carbohydrate ether bonds under alkaline pulping conditions has also been observed in model experiments[11,12]. However, based on his finding that enzyme lignins isolated from wood and kraft pulp gave similar results on methylation, Minor[9] ruled out the probability of the formation of lignin-carbohydrate ether bonds during kraft pulping.

Factors other than lignin-carbohydrate linkages may also be responsible for the resistance of the residual lignin to delignification. By analyzing acidolysis monomeric products originating from β-aryl ether substructures in the residual lignin in a kraft pulp, Gellerstedt *et al.*[13] suggested that the rather low content of β-aryl ether substructures in the residual lignin might be at least in part responsible for the observed resistance of the residual lignin to delignification.

In the work presented in this paper, residual lignins were isolated from unbleached and semi-bleached kraft pulps and were characterized for a better understanding of the chemical changes in residual lignin during the first two stages of bleaching and for gaining some insights into the cause for its resistance to delignification. For comparison, a lignin preparation was also isolated from the alkaline-extraction stage effluent.

RESULTS AND DISCUSSION

Isolation and Purification of Residual Lignins

Residual lignins were isolated from unbleached and semibleached (after chlorination and extraction) southern pine kraft pulps by selectively hydrolyzing polysaccharides with cellulolytic enzymes as described in the previous study[1]. The residual lignin from the unbleached pulp (hereafter referred to as RL-UB) was recovered as an insoluble residue after enzymatic treatment. On the other hand, a part of the residual lignin from semibleached pulp (RL-SB) became solubilized during the enzymatic treatment and was recovered by acidification to pH 2.5. Thus RL-SB was obtained in two fractions, one which became solubilized

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Table 1. Lignin yield and nitrogen content.

Sample	Total nitrogen (%) a	b	Lignin yield (%) c
RL-UB	2.50	0.58	80.7
RL-SB-I	7.30	2.26	34.9
RL-SB-II	7.20	3.11	27.3

a -- before purification
b -- after purification
c -- after purification, based on Klason lignin contents (calculated as 0.15 times Kappa number) of starting pulps.

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during the enzyme treatment (RL-SB-I) and one which remained as an insoluble residue during enzyme treatment (RL-SB-II). For comparison, chlorinated lignin in the alkali extraction filtrate (AEL) was also isolated by acidification and precipitation.

All three residual lignin samples, RL-UB, RL-SB-I and RL-SB-II contained substantial amounts of nitrogen, indicating enzyme contamination. Thus, these three samples were purified and the results are given in Table 1. As can be seen, the purification was only partially successful, especially for the two RL-SB fractions. The overall lignin recovered, based on lignin in the original pulps, was relatively high, being over 80% for RL-UB and 60% for the two RL-SB fractions combined.

Klason Lignin and Sugar Composition

Klason lignin contents and carbohydrate compositions of the four lignin preparations are listed in Table 2.

The sugar contents of these lignins are similar in magnitude to that of a residual lignin preparation[1] purified by liquid-liquid extraction.

The residual lignins RL-UB, RL-SB-I and RL-SB-II are contaminated to various extents with the enzymes which in a crude form contain roughly 40% carbohydrates. Therefore, there is a possibility that the carbohydrates associated with the residual

Table 2. Klason lignin content and sugar composition.

Compound	RL-UB	AEL	RL-SB-I	RL-SB-II	Cellulase Enzyme
Klason lignin	94.9	85.1	79.3	85.6	-
Total sugar*	5.4	8.7	4.6	2.6	39
Arabinose**	1.3	0.7	3.7	3.5	13.3
Xylose**	10.0	2.5	21.8	21.2	9.2
Mannose**	5.7	0.7	8.1	7.3	17.7
Galactose**	71.7	58.3	50.1	37.4	45.5
Glucose**	11.3	37.8	16.3	30.1	13.9

*-- based on oven-dried samples
**-- based on total sugars

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lignins are introduced by enzyme treatments. However, the compositions of the carbohydrates in the residual lignins are quite similar to that of those found in the alkali lignin. The alkali extraction lignin (AEL) has not been subjected to any enzymatic hydrolysis and contains even a larger amount of carbohydrates. Therefore, it is unlikely that the carbohydrates are introduced by the enzymatic treatments and thus must be of wood origin.

There is another possibility that the carbohydrates are bound to the residual lignins by strong physical adsorption due to their polymeric nature. Experimental results[1] show, however, that such adsorption is unlikely to occur between cellulosic fibers and lignins. Furthermore, non-selective physical adsorption cannot explain the enrichment of galactose which exists either as single-sugar-unit side chains in galactoglucomannans or as 1,4-linked galactans in pectin. The latter is alkali soluble and is not expected to survive under alkaline pulping conditions.

Another possibility is that the residual lignins are covalently linked to the carbohydrates in pulp as proposed by Yamasaki *et al.*[1] and Minor[9]. Formation of alkali-stable carbon-carbon bonds between lignin and carbohydrates via aldol

condensation[10], formation of stable lignin-carbohydrate ether bonds[11], and high stability of benzyl ether bonds between lignin and carbohydrates[8] have been observed under alkaline pulping conditions or in model experiments. Therefore, it is most probable that the carbohydrates are covalently linked to the residual lignins. Such bonds can well explain the difficulty in complete delignification of kraft pulps.

It is interesting to note that galactose in all lignin preparations is the predominant constituent of the carbohydrates. While linkages between galactose and lignin were postulated to be dominant in the lignin-carbohydrate complex[4-6], Minor[9] has recently shown that oligomers of 1,4-linked galactan were covalently bonded to residual lignin in pulp. A particularly high content of galactose was also found in spent liquors from both chlorination and alkaline extraction[14].

It should be noted that the enrichment of galactose in enzyme treated lignin may be due partly to the fact that the crude cellulases do not efficiently hydrolyze the 1,4-linked galactan structure.

The relatively large amounts of glucose present in all samples suggest that 1) glucose exists in oligomers of hemicelluloses linked to lignin via other sugar units rather than glucose, and/or 2) glucose is linked directly to lignin. Although direct evidence confirming chemical linkages between lignin and cellulose in wood has not been found, they cannot be ruled out [6]. Addition of ionized hydroxyl groups in carbohydrate fragments to epoxide intermediates formed by alkali-assisted cleavage of β-aryl ether bonds in non-phenolic lignin units[11,12] can bring about formation of lignin-cellulose linkages during alkaline pulping. The enrichment of glucose and the decrease of galactose in lignin samples isolated from the semibleached pulp even give more weight to the second explanation.

It is also interesting to note that the ratios of the amount of arabinose to that of xylose in all three residual lignin samples, ranging from 0.13 to 0.17, are close to the ratio in arabinoglucuronoxylans (0.13). In addition, both sugars are

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Table 3. Elemental composition, methoxyl and carboxylic contents

Percentage	RL-UB	AEL	RL-SB-I	RL-SB-II
C*	62.48	49.98	48.34	53.56
H*	5.66	3.77	4.17	4.86
O*	30.78	32.83	39.31	34.99
S	0.96	0.53	1.66	1.22
Cl*	ND	12.84	6.11	5.01
N	0.58	0.22	2.26	3.11
Methoxyl	14.88	2.59	2.47	3.71
Carboxylic	2.40	11.92	11.62	10.92

* -- corrected for protein, sugar, and ash contents
ND -- not determined

enriched in the preparations isolated from the semibleached pulp. This implies that both arabinose and xylose might also be covalently linked to the residual lignin.

Chemical Analyses

The elemental compositions, methoxyl and carboxylic acid contents of the four lignin preparations are given in Table 3.

Elemental composition and methoxyl content of residual lignin RL-UB are similar to those of typical softwood kraft lignins [15]. The extremely low methoxyl contents and the high carboxylic contents of AEL, RL-SB-I and RL-SB-II provide evidence that during prebleaching (chlorination and extraction stage), residual lignin in pulp underwent extensive oxidation and demethylation. This conclusion is also supported by IR and NMR spectral data.

Elemental analysis showed that all lignin preparations contain sulfur. Sulfur contents of lignin samples RL-UB, RL-SB-I and RL-SB-II are in the neighborhood of that of typical softwood kraft lignins[15]. Proteins generally contain 0.3-2.0%, with an average of 1.0%, sulfur[16]. The ratio of nitrogen to sulfur of the

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enzymes used was found to be 11.3. Thus, amounts of sulfur contributed by the proteins present in the samples are only small fractions of the total sulfur. Therefore, the presence of sulfur is a good indication that the cooking liquor has already been in contact and reacted with the residual lignin in the unbleached kraft pulp during kraft pulping.

Considerable amounts of chlorine exist in all isolated lignin preparations except RL-UB, indicating that residual lignin has been subjected to chlorine substitution, in addition to oxidation, to a noticeable degree. The amounts of chlorine found in the samples are close to previously reported values[14,17].

CP/MAS ^{13}C NMR Analysis

CP/MAS ^{13}C NMR spectra were obtained for samples RL-UB and RL-SB-II in the solid state. The spectrum of RL-UB is typical of kraft lignin with prominent resonances for phenolic (147 ppm), aromatic (106-140 ppm) and aliphatic carbons (60-85 ppm). In addition, there is a tangible presence of aliphatic carbons in 30-50 ppm range. A comparison of the spectra of RL-UB and RL-SB-II shows that in the residual lignin after CE stages (RL-SB-II), the methoxyl and phenolic contents are significantly reduced. In the spectrum of RL-SB-II, the carboxyl resonance (170-180 ppm) is evident and the aliphatic carbon resonances (20-50 ppm) become relatively dominant; these could be partly due to contamination by degraded proteins from the cellulases. The differences in methoxyl and carboxyl groups present in RL-UB and RL-SB-II as indicated by the NMR data agree with chemical analysis data in Table 3.

Molecular Weight Distribution

Molecular weight distributions of lignin preparations RL-UB, AEL, RL-SB-I and RL-SB-II are shown in Figure 1. As a reference, the molecular weight distribution of a lignin preparation isolated from a kraft black liquor is also given in the same figure.

It can be observed that the average molecular weights of the residual lignin RL-SB-I and RL-SB-II are very similar to that of

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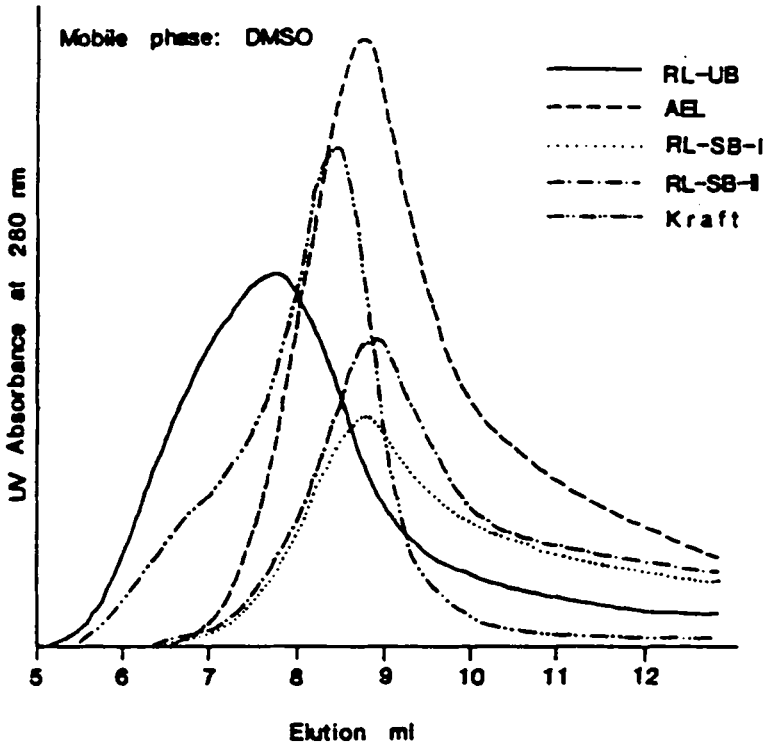

Figure 1. Molecular Weight Distribution Curves

the alkali lignin AEL, but considerably lower than that of the kraft lignin. This indicates that lignins AEL, RL-SB-I and RL-SB-II were all extensively degraded to a similar degree during prebleaching.

The average molecular weight of residual lignin RL-UB is higher than that of the kraft lignin, confirming that the residual lignin in the unbleached kraft pulp is degraded to a less extent than the kraft lignin as proposed by Yamasaki et al.[1]. This is probably due to the presence of stable lignin-carbohydrate linkages at the α-position, which retards the hydrolysis of the adjacent β-ethers as shown by Taneda et al.[8].

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It is interesting to note that although all four lignin preparations are soluble in aqueous alkaline solutions and the average molecular weights of RL-SB-I and RL-SB-II are very similar to that of AEL, RL-SB-I and RL-SB-II could not be extracted out of the pulp during alkali extraction. Since physical adsorption is unlikely as discussed previously, the most reasonable explanation for the non-extractability of RL-SB-I and RL-SB-II might be that they are chemically bonded to the carbohydrates. It is these chemical linkages that prevent the residual lignins from being removed during pulping and prebleaching. The fact that some carbohydrates survived the enzymatic hydrolysis also supports this explanation.

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SUMMARY AND CONCLUSIONS

All four lignin preparations are readily soluble in aqueous alkaline solutions. All the residual lignins contain sulfur in an amount similar to that of typical technical kraft lignin.

The residual lignin isolated from the unbleached kraft pulp appears to have characteristics similar to that of typical softwood kraft lignins. In contrast, much higher carboxylic acid contents and much lower methoxyl contents were found in the other three lignin preparations.

The average molecular weights of the residual lignins RL-SB-I and RL-SB-II isolated from the semibleached kraft pulp were found to be similar to that of the alkali extraction lignin (AEL) isolated from the extraction spent liquor and lower than that of the kraft lignin. On the other hand, the average molecular weight of the residual lignin (RL-UB) isolated from the unbleached kraft pulp was found to be higher than that of the kraft lignin.

Appreciable amounts of carbohydrates were found in all lignin preparations. Galactose was the most abundant component, with glucose and xylose being the other two major constituents. Lignin preparation AEL has a higher carbohydrate content than the others.

It is therefore concluded that the carbohydrates are most likely linked to the residual lignins by covalent bonds as

proposed by Yamasaki et al.[1], and this chemical bonding is the most probable cause for the resistance of the residual lignin to further delignification during kraft pulping and prebleaching. The residual lignins are probably linked to the carbohydrates mainly via hemicelluloses, in particular, galactose units. However, direct linkages between residual lignins and the cellulose cannot be ruled out.

EXPERIMENTAL

Preparation of Pulps

Commercially-available chips (3000 g OD) of loblolly pine (Pinus taeda L.) were treated in a one-cubic-foot digester equipped with a circulation pump and a three-pass heat exchanger. The chips were evacuated for 30 minutes and then the cooking liquor was sucked into the digester. The cooking conditions were: 19.5% active alkali (as Na_2O on OD wood), 25% sulfidity, 4:1 liquor to wood ratio, cooking temperature 170°C, time to temperature 90 minutes, and time at temperature 110 minutes. At the end of a cook, the content of the digester was blown into a blow tank. The pulp was washed thoroughly and screened in a laboratory flat screen with an eight-cut plate. Three cooks of pulp were produced and mixed after screening. The average screen yield was 46.4%, and the average rejects 0.9%. The Kappa number of the combined kraft pulp was 30.1.

The chlorinated pulp was obtained by treatment of the kraft pulp with an aqueous chlorine solution. The chlorination conditions were as follows: available chlorine (on OD pulp) 6.0%, pulp consistency 3.5%, reaction temperature 25°C, and reaction time 60 minutes. The chlorinated pulp was washed with water until the filtrate became colorless and neutral. The average Kappa number of the chlorinated pulp was 13.4.

Alkaline extraction of the chlorinated pulp was conducted under the following conditions: alkali charge (on OD pulp) 3.0%, pulp consistency 10.0%, reaction temperature 70°C, and extraction

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time 120 minutes. The extracts were collected by centrifugation, combined, and filtered through a sintered glass crucible of medium porosity. The filtrate was acidified to pH 2.5 with HCl and centrifuged. The precipitates were washed twice with dilute HCl (pH 2.5) and finally freeze-dried from a water suspension to yield the alkali extraction lignin (AEL). The pulp was washed with water thoroughly. The average Kappa number of the semibleached pulp was 5.0.

Cellulolytic Hydrolysis of Pulps and Isolation of Residual Lignins

The experimental approach for isolation of the residual lignins is shown in Figure 2.

The pulps were beaten to 260 ∿ 300 Canadian Standard Freeness in a laboratory Hollander beater, acording to TAPPI Method T 200 OS-700, prior to enzymatic hydrolysis.

In each of four 500-ml flasks, 20 g pulp (OD), at a consistency of about 25%, was treated with 320 ml enzyme buffer solution, which was prepared by dissolving 1.2 g Cellulases TV concentrate (crude powder from Miles Labs., Inc.) into 320 ml buffer solution at pH 4.2 (6.56 g sodium acetate and 4.64 ml acetic acid dissolved in 4 l distilled water). After incubation in a shaking water bath at 45°C for three days, the hydrolysates were removed by centrifugation. The residues from two flasks were combined and placed into one flask, and then subjected to a second enzymatic treatment under the same conditions as the first treatment. After the second treatment, the residues from two flasks were combined again and placed into one flask, and treated with the enzyme buffer solution under the same conditions. The fourth treatment was carried out by the same procedure as was the third, except that only 0.6 g instead of 1.2 g of cellulases was used. The residues from the fourth treatment were washed twice with dilute HCl (pH 2.5) and freeze-dried from a water suspension to give the water-insoluble residual lignins.

During the successive enzymatic hydrolyses some residual lignin in the semibleached pulp became soluble in the buffer

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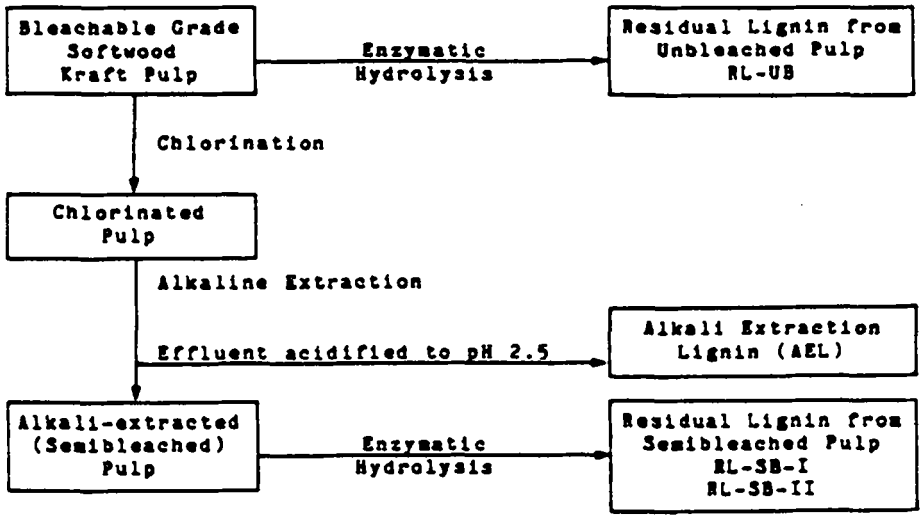

Figure 2. Experimental Approach

solution. This water-soluble residual lignin was isolated by combining the hydrolysates from four treatments then acidifying to pH 2.5 with HCl. The precipitate was centrifuged, washed twice with dilute HCl (pH 2.5), and finally freeze-dried. Thus, two lignin preparations were isolated from the semibleached pulp: fraction I from the hydrolysates by acidification and fraction II, from the insoluble residues.

Purification of the Residual Lignins

All crude residual lignins were contaminated with enzymes to varying extents. A suitable purification method was thus investigated. Among gel filtration, selective precipitation of the enzymes, proteolytic hydrolysis using various proteinases, and alkali-catalyzed hydrolysis under different conditions, the procedure described below was found to be the most effective one and employed.

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The crude residual lignins were dissolved in 1N NaOH in a lignin concentration of 1.0%, and stirred mechanically at room temperature for two hours. After centrifugation, the precipitates were washed with 1N NaOH and then discarded. The washing and the supernatants were combined and acidfied to pH 2.5 with HCl. The precipitates were centrifuged, washed with dilute HCl (pH 2.5), and then freeze-dried.

After the extraction, the residual lignins were treated with 2N NaOH, in a lignin concentration of 1.0%, at 70°C in a water bath under a nitrogen atmosphere. After being stirred mechanically under these conditions for 48 hours, the solution was neutralized with acetic acid, and then transferred into a dialysis tubing with a molecular weight cutoff of 1000. The contents of the tubing were dialyzed against distilled water for 48 hours, dilute acetic acid (pH 3.0) for 24 hours, and then again distilled water for another 24 hours. During the dialysis, the distilled water or the dilute acetic acid was changed regularly. The purified residual lignins were recovered by freeze-drying the dialyzed solution.

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Chemical Analyses

Elemental analyses, carboxyl, and methoxyl content determinations were carried out by E+R Microanalytical Laboratory, Corona, NY 10189.

Elemental compositions were corrected for ash, protein and sugar contents. The elemental composition of protein was assumed as follows: 48.0% C, 6.5% H, 16.0% N, 29.5% O^{18}. Elemental conposition of pentosans was calculated as: 45.45% C, 6.06% H, 48.49% O, and hexosans as: 44.44% C, 61.7% H, 49.38% O.

Klason Lignin and Carbohydrate Contents

The Klason lignin content and carbohydrate content of the purified lignin samples were measured according to the alditol acetate procedure[19]. The hydrolysis survival factors and the slopes of the calibration curves used are given in Table 4.

Table 4. Hydrolysis survival factors and slopes of the calibration curves.

	H	K
Arabinose	0.6398	1.2813
Xylose	0.9097	1.1236
Mannose	1.2462	1.0891
Galactose	0.4486	0.8526
Glucose	0.8035	0.8896

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Molecular Weight Distribution

Size exclusion chromatography was used to examine the molecular weight distribution of residual lignins under the following conditions:

Columns: silica size mixing column (SE-60, 100, 500, 1000, 4000; μ-Porasil (60A); μ-Bondagel (E-125)

Mobile Phase: Dimethyl Sulfoxide at 50°C

Flow Rate: 0.2 ml/min

Detection: UV (280 nm)

Sample: 0.1% in DMSO

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