

ISOLATION AND CHARACTERIZATION OF LIGNIN FROM PREHYDROLYSIS LIQUOR OF KRAFT-BASED DISSOLVING PULP PRODUCTION

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Lignin separation from the prehydrolysis liquor (PHL) resulting from dissolving pulp production will create new revenue for the dissolving pulp sector, fitting well into the integrated forest biorefinery concept. Lignin will likely become a valuable source of renewable energy (e.g. biofuel) and biomaterials (e.g. plastics, adhesives). In this study, lignin was isolated from PHL by acidification with a dilute H₂SO₄ solution, followed by purification through dissolution in a dioxane solution (9:1) and re-precipitation with diethyl ether. The characteristics of PHL lignin were compared with those of the dioxane lignin isolated from hardwood (maple, poplar and birch wood chips, in a ratio of 7:2:1), which is the raw material used for dissolved pulp production. Thus, the obtained lignin samples were characterized by UV, FTIR, ¹H-NMR spectroscopy, molecular weight determination, elemental and methoxyl analyses. The absorptivity of hardwood lignin at 276 nm was of 10.0 l g⁻¹cm⁻¹, while that of PHL lignin was of 17.2 l g⁻¹cm⁻¹. The presence of condensed structures in PHL lignin (intense bands at 870 and 890 cm⁻¹ in the FTIR spectrum) was observed. The lignin isolated from PHL has low molecular weight, and a low methoxyl group per C₉ unit, in comparison with other lignin samples. ¹H-NMR data indicate a significant increase of the phenolic hydroxyl content in PHL lignin, caused by the cleavage of the aryl-ether bonds during prehydrolysis. Based on these results, it can be concluded that the lignin isolated from PHL may have a potential for polymer industry.

Keywords: PHL lignin, dissolving pulp process, phenolic hydroxyl group, molecular weight, methoxyl group

INTRODUCTION

For the production of dissolving pulp from the kraft process, wood chips must be pretreated with steam or hot water to remove hemicelluloses, which is known as the prehydrolysis step. In this process, significant amounts of organics, such as hemicelluloses, lignin and acetic acid are dissolved in the prehydrolysis liquor (PHL). The recovery and potential use of these dissolved organics would fit well into the forest biorefinery concept for kraft-based dissolved pulp production.^{1,2} As part of the organics dissolved in PHL,³⁻⁴ lignin may be utilized as a raw material for many value-added products, e.g. phenol, bio-

fuel and plastics, thus generating additional revenue to the pulp and paper industry.⁵

During prehydrolysis, lignin depolymerization occurs, which may result in the cleavage of the lignin-carbohydrates bonds.⁶ Also, re-polymerization/condensation can occur slowly, because of the increased content of C-C condensed structures evidenced by the analysis of lignin isolated after steam explosion of aspen wood,^{7,8} and of the decreased content of β -O-4 structures. The main inter-unit β -O-4 aryl ether linkages are cleaved under acidic conditions, with the release of the free phenolic hydroxyl group.^{9,10}

Early studies on methanol-extracted lignin from steam-exploded aspen (*Populus tremuloides*) indicated cleavage of the β -O-4 aryl ether linkages, causing a decrease in molecular weight and an increase in the phenolic content.¹¹ Results from beech wood lignin also showed that molecular weight decreased with increasing temperature while, above 215 °C, condensed structures began to form.¹² In the present paper, lignin was isolated from the prehydrolysis liquor (PHL) of a kraft-based dissolving pulp production process developed in Eastern Canada. The isolated lignin was characterized by UV, FTIR and ¹H-NMR spectroscopy, molecular weight and elemental analyses.

EXPERIMENTAL

Raw materials

Maple, poplar and birch wood chips, collected from a mill in Eastern Canada in a ratio of 7:2:1, were ground (40/60 mesh) in a Wiley mill, extracted with acetone and vacuum-dried over P₂O₅. The prehydrolysis liquor (PHL) was collected from the same mill.

Isolation of lignin from PHL

The collected PHL was acidified to pH 2, by using a dilute H₂SO₄ solution, and lignin was precipitated and separated by centrifugation. The lignin sample collected was thoroughly washed.

Isolation of lignin from wood meal

The procedure applied in an earlier study¹³ was followed. The acetone extractive-free wood meals were refluxed with an acidic dioxane (9:1) solution. HCl concentration in the dioxane solution was of 0.2 N. The dioxane solution-to-wood meal ratio was 8. The wood meal was refluxed with a dioxane solution for about 1 h, in N₂ atm. Upon completion, the wood meal dioxane mixture was filtered on a Buchner funnel and the residue was washed with a dioxane solution (9:1), after which it was neutralized by adding solid Na₂CO₃ and filtered. The filtrate was concentrated in a vacuum evaporator at 50 °C, and a concentrated dioxane solution was added dropwise, to precipitate the lignin. The lignin precipitate was washed and vacuum-dried over P₂O₅.

Lignin purification

The crude lignin isolated from wood meal and PHL was dissolved in dioxane (9:1), and again precipitated in ether, under constant stirring with a magnetic bar. The precipitated lignin was dried in vacuum over P₂O₅.

Acetylation

The lignin sample obtained as described above (100 mg) was added separately to 2 mL of dry pyridine-acetic anhydride (1:1) and kept for 72 h. The solution

was added to a 10-fold volume of ice-cold water, and the acetylated lignin was recovered as a precipitate, subsequently purified by successive washing with water and dried under vacuum over P₂O₅.

Determination of lignin molecular weight

The weight-average (M_w) and number-average (M_n) molecular weight of the acetylated lignin was determined by GPC, on a Sodex KF-802.5 column. The samples were dissolved in tetrahydrofuran (THF) and 10 μ L were injected. The column was operated at 30 °C and eluted with THF at a flow rate of 1 mL min⁻¹. Calibration was done using polystyrene standards.

Elemental analysis

C, H, O and N analyses were carried out on a LECO CHN analyzer. The methoxyl content of dioxane lignin was determined in accordance with a Japanese International Standard Method (JIS P8013 1972).

Spectroscopy

Ultraviolet: 7-8 mg dioxane lignin was dissolved in 100 mL dioxane (9:1), followed by twice repeated dilution, and the spectra were recorded using a GENESYS 10S spectrophotometer.

FTIR: IR spectra were recorded with a Shimadzu FTIR spectrometer model 8201PC. The dried samples were embedded in KBr pellets, at concentrations of about 1 mg/100 mg KBr. The spectra were recorded in the absorption band mode in the 4000-400 cm⁻¹ range.

The ¹H NMR spectra were recorded for solutions of 100 mg acetylated lignin contained in 0.5 mL CDCl₃, using the solvent as an internal standard. For quantification of protons, the signals of some specified regions of the spectrum were integrated with respect to a spectrum-wide baseline drawn at the level of the background noise, and the results were referred to the signal for methoxyl protons, whose average number per C₉ unit was established as described above.

RESULTS AND DISCUSSION

The amount of lignin found in PHL was of about 1%, which represents about 20% of the total solid content of PHL.^{3,14} The lignin content in PHL depends on the intensity of prehydrolysis conditions.^{3,15} Yoon *et al.*¹⁶ obtained 5.11 % lignin (based on wood) in loblolly pine prehydrolyzed for 90 min at 190 °C. The lignin content in the hot-water extract of sugar maple was of 3.27% (based on wood).¹⁷ Leschinsky *et al.*⁶ also reported that lignin is degraded and dissolved during the prehydrolysis process, and Liu *et al.*¹⁸ observed that, upon prehydrolysis, lignin density increased on the external surface of wood chips. It is expected that the lignin dissolved in PHL would show fewer chemical/

structural changes, similarly to organosolv lignin, but unlike kraft or sulphite lignin. Masura¹⁹ observed that the Klason lignin content of prehydrolyzed beech wood decreased in the first hour of prehydrolysis, at 160-170 °C, indicating lignin dissolution during prehydrolysis. The amount of extractable lignin in auto-hydrolysis was very high at a high temperature (e.g. 195-215 °C).⁷ A reason for the enhanced delignification observed for auto-hydrolysis is the cleavage of the aryl-ether bonds, resulting in lignin depolymerization and a high content of phenolic hydroxyl groups.

Elemental analysis

Based on the elemental analysis of the lignin samples listed in Table 1, a possible empirical composition of PHL lignin was $C_9H_{9.14}O_{3.68}(OCH_3)_{1.04}$, while that of dioxane lignin from the mixed hardwood was $C_9H_{10.52}O_{3.36}(OCH_3)_{1.20}$. This indicates that the lignin in PHL has a lower methoxyl content, and that demethylation occurred during prehydrolysis. Similar results were observed in aspen steam-exploded lignin.¹¹ Leschinsky *et al.* also observed that the methoxyl per C_9 of the lignin precipitated

from the prehydrolysate was lower than that in the MWL of *Eucalyptus globulus*.²⁰

UV spectroscopy

Figure 1 shows that dioxane lignin had a well-defined maximum at 276 nm, while the PHL lignin had another peak at 276 nm, even though wider, originating from the non-condensed phenolic groups in lignin. As known, the guaiacyl structures, especially those from softwood, exhibit maxima in the 280 region. However, substitutions of an extra methoxyl group in the 5th position shift the maxima to lower wavelength,²¹ therefore both lignin samples here involved are rich in syringyl units. The absorptivity of dioxane lignin was of $10.0 \text{ l g}^{-1}\text{cm}^{-1}$, while that of PHL lignin was of $17.2 \text{ l g}^{-1}\text{cm}^{-1}$, as presented in Table 2. The absorptivity of beech lignin obtained from steam explosion was of $15.60 \text{ l g}^{-1}\text{cm}^{-1}$ at 277 nm.²² The typical shoulder at 310-320 nm was absent in these lignin samples, indicating the absence of ester or ether bonds between hydroxycinnamic acids, such as *p*-coumaric acid and ferulic acid of lignin. Some juvenile hardwood lignin and non-wood lignin show the presence of these bands.^{13, 23-24}

Table 1
Elemental analyses, methoxyl contents and C_9 formula of PHL and dioxane lignin

Lignin sample	C	H	O	OCH ₃	C_9 formula*
PHL	57.8	5.77	35.5	15.2	$C_9H_{9.14}O_{3.68}(OCH_3)_{1.04}$
Hardwood	58.0	6.59	34.6	17.8	$C_9H_{10.52}O_{3.36}(OCH_3)_{1.20}$

*Empirical formula of $C_xH_yO_z(OCH_3)_n$, were calculated as follows: $n = (\%OCH_3)/31.04$; $x = (\%C)/12 - n$; $y = (\%H) - 3n$; $z = (\%O)/16 - n$

Table 2
UV characteristics of dioxane and PHL lignin

Lignin	Wavelength at max. (nm)	Absorptivity at max. ($\text{l g}^{-1}\text{cm}^{-1}$)
Dioxane lignin	276	10.0
PHL lignin	276	17.2

Table 3
Average molecular weight and polydispersity of dioxane and PHL lignin

Sample	Mw	Mn	Polydispersity (Mw/Mn)
Hardwood	6521	1638	4.0
PHL	2975	794	3.7

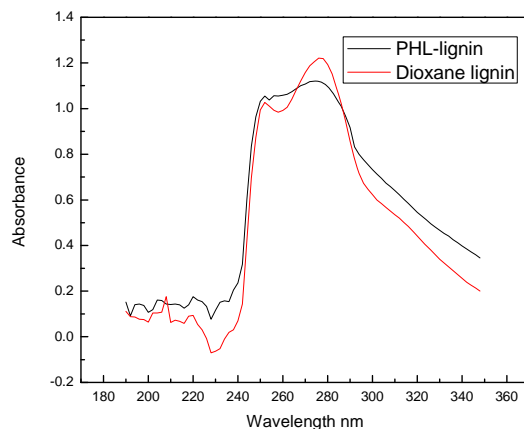


Figure 1: UV spectra of PHL and dioxane lignin

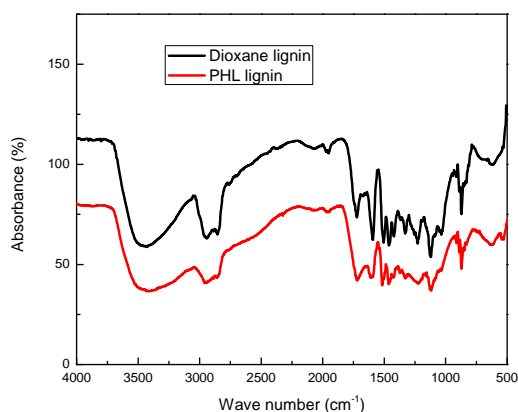


Figure 2: FT-IR spectra of PHL and dioxane lignin

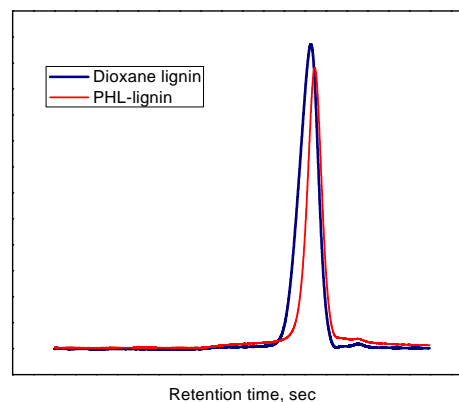


Figure 3: Chromatogram of PHL and dioxane lignin

FTIR spectroscopy

To elucidate the structure of lignin, the FTIR spectra of PHL and dioxane lignin samples were recorded, and shown in Figure 2. The band at 1330 cm^{-1} is due to the presence of the phenolic OH group, whereas the band at 1030 cm^{-1} is characteristic of a primary alcohol,²⁵ which is weaker in PHL lignin than in dioxane lignin. The bands at 1330 , 1220 and 1120 cm^{-1} correspond to the syringyl unit, whereas the small shoulders at 1275 , 1153 and 1037 cm^{-1} are assigned to the guaiacyl unit of lignin molecules,²⁶ again, much weaker in PHL lignin. The band at 1504 cm^{-1} was shifted to 1515 cm^{-1} on PHL lignin, which is probably caused by the decreased amount of β -*O*-4 linkages.⁶ These results suggest that the prehydrolysis process cleaves the β -*O*-4 linkages of lignin. The $1594/1510$, $1463/1510$ and $1418/1510$ ratios are lower in PHL lignin than in dioxane lignin, indicating that the syringyl-to-guaiacyl ratio decreased during prehydrolysis.²⁷

Similar results were observed in the lignin sample from the water prehydrolysis of *Eucalyptus globulus* wood.⁶ The presence of condensed structures in PHL lignin is indicated²⁸ by the stronger bands at 870 and 890 cm^{-1} .

Molecular weight

The molecular weight distribution of PHL and dioxane lignin samples was measured by GPC (Fig. 3), and weight-average molecular weight (Mw), number-average molecular weight (Mn) and polydispersity (Mw/Mn) are shown in Table 3. The results obtained reveal that a substantial degradation of lignin occurred during prehydrolysis. The Mw of the lignin isolated from PHL was remarkably lower than that of wood lignin (about 3000 vs. 6500). The molecular weight of PHL lignin depends on prehydrolysis intensity. Bentivenga *et al.* showed²² that extensive degradation of the steam-exploded lignin occurred. Mitsuhiro²⁹ showed that the

molecular weights (Mw) of exploded lignin decreased with increasing steam pressure and time.²⁹

¹H-NMR

The integrated NMR spectra obtained for acetylated PHL and dioxane lignin are shown in Figure 4, while Table 4 lists the signal assignments according to an early reference of Lundquist.³⁰ The rapid increase of the phenolic hydroxyl content in PHL lignin, shown in Table 4, indicates extensive cleavage of the aryl-ether

bonds during prehydrolysis. The aliphatic hydroxyl content in PHL lignin is much lower than that of dioxane lignin. It can be assumed that the elimination of the primary and secondary aliphatic hydroxyls is a result of the aryl-ether cleavage mechanism, which agrees with the results for the prehydrolysis lignin of *Eucalyptus globulus*.⁶ Li and Lundquist reported³¹ that hydrolysis under slightly acidic conditions can bring about the loss of aliphatic OH groups through the homolytic cleavage of the C_β-O bond.

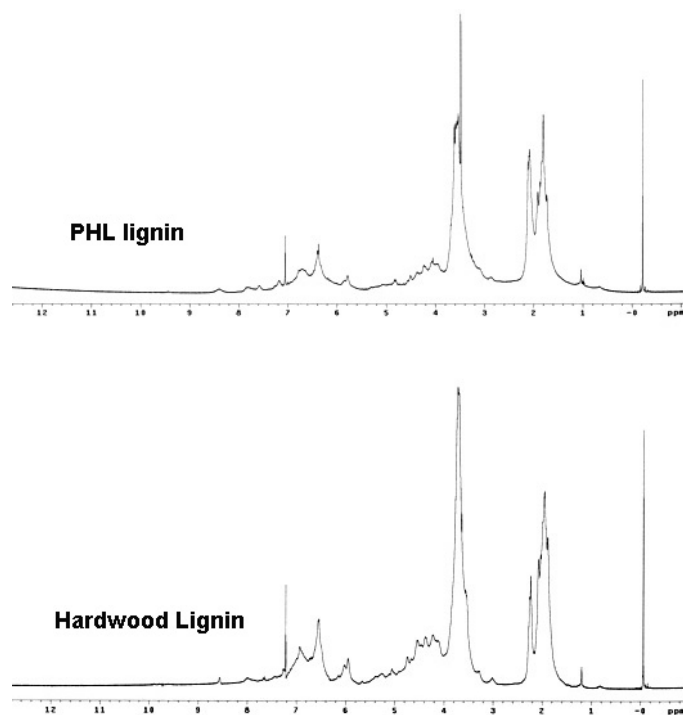


Figure 4: ¹H-NMR spectra of PHL and dioxane lignin

Table 4

Assignments of signals and protons per C₉ structural unit in the ¹H NMR spectra of acetylated lignin

Range (ppm)	Main assignments	PHL lignin	Dioxane lignin
7.25-6.80	Aromatic proton in guaiacyl units	0.58	0.64
6.80-6.25	Aromatic proton in syringyl units	0.52	0.75
6.25-5.75	H _α of β-O-4 and β-1 structures	0.26	0.41
5.75-5.24	H _α of β-5 structure	0.29	0.31
5.20-4.90	H of xylan residue	0.20	0.19
4.90-4.30	H _α & H _β of β-O-4 structures	1.16	1.09
4.30-4.00	H _α of β-β structures		
	H of xylan residue		
4.00-3.48	H of methoxyl groups	3.12	3.60
2.50-2.22	H of aromatic acetates	1.16	0.51
2.22-1.60	H of aliphatic acetates	1.88	2.55
Total proton per C ₉ structural unit		9.17	10.05

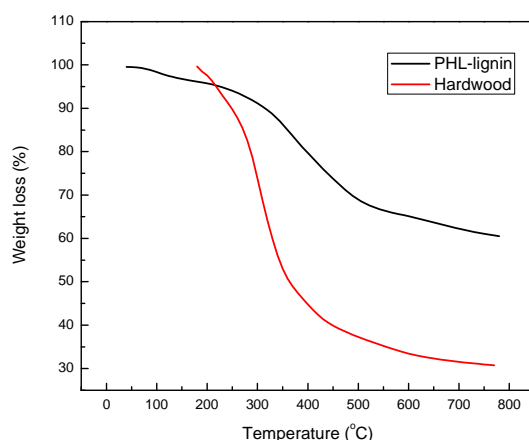


Figure 5: Thermal degradation of PHL and dioxane lignin

According to the $^1\text{H-NMR}$ spectra (Fig. 4), both dioxane and PHL lignin samples were shown to have a total number of 1.39 and 1.10 aromatic protons (6.25-7.25 ppm) per C_9 unit, respectively. The methoxyl content in PHL lignin was lower than that in dioxane lignin, indicating demethylation of the aromatic methoxyl groups in the lignin structure during prehydrolysis. Similar results were obtained for lignin from steam-exploded lignocellulosic biomass.³²

Thermogravimetric analysis

The TGA results illustrated in Figure 5 show that PHL lignin was more thermally stable than the dioxane lignin over the 200-450 °C temperature range. Dioxane lignin showed a nearly 40% weight loss at temperatures below 335 °C while, at 550 °C, the PHL lignin had a weight loss of about 30% (Fig. 5). The degradation of dioxane lignin began earlier and was smoother than that observed for PHL lignin, suggesting that the degradation rate of dioxane lignin was faster than that of PHL lignin, under the conditions studied. A better thermal stability of PHL lignin indicates its suitability in polymer processing.

CONCLUSIONS

The present study demonstrates that the prehydrolysis step of kraft-based dissolving pulp production removes a part of the lignin and alters its structure. Lignin demethylation is supported by a lower methoxyl content of PHL lignin, comparatively with wood lignin. In addition, PHL lignin has a low molecular weight, indicating depolymerization of lignin during prehydrolysis.

The main inter-unit $\beta\text{-O-4}$ aryl ether linkages are also cleaved, resulting in an increased free phenolic hydroxyl group content, which may facilitate further utilization of PHL lignin for other products, such as phenolic resin. The isolated PHL lignin is more thermally stable. Its characteristics permit the conclusion that PHL lignin would be a suitable raw material in producing biomaterials.

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