

Structural Changes of Lignin during Kraft Pulping of Eucalyptus Tereticornis

K.S. Bhandari and Anju Bhatnagar

Cellulose and Paper Division, Forest Research Institute, Dehradun -248006, Uttaranchal

ABSTRACT

Dioxane lignin from Eucalyptus tereticornis wood and its kraft pulps with kappa number of 44.91 and 26.46 was isolated and subjected to elemental composition, functional groups analysis, IR spectroscopy and alkaline nitrobenzene oxidation studies. Elemental composition of the lignin and empirical formula derived from these values revealed that wood lignin contains lower amount of carbon and higher amount of hydrogen and oxygen as compared to pulp lignin. Methoxyl, alcoholic hydroxyl and phenolic hydroxyl content were decreased on pulping. IR spectroscopic studies also indicated the decrease in methoxyl content. Carbonyl and carboxyl groups were increased on pulping. On alkaline nitrobenzene oxidation of lignin, eight compounds namely p-hydroxy benzoic acid, vanillic acid, syringic acid, p-hydroxy benzaldehyde, vanillin, syringaldehyde, aceto vanillone, acetosyringone were identified by HPLC, quantitatively. The results are discussed in the paper at adequate length.

INTRODUCTION

Studies concerning structure of lignin in raw material are of importance for the evaluation of delignification/dissolution behavior during pulping. Structural evaluation of residual lignin in unbleached pulps impart understanding to optimize the pulping parameters for industrial delignification, fibre bleachability, interfibre bonding and several other physical, optical and mechanical properties of pulps. Determination of the amount and nature of residual lignin in unbleached pulps is important for both pulping and bleaching researches.

In the present studies, dioxane lignin from wood and its kraft pulps of 44.91 and 26.46 kappa numbers was isolated and subjected to elemental composition, functional group determination, IR spectroscopy and alkaline nitrobenzene oxidation studies to assess the structural modifications occurred in lignin during the kraft pulping of E.tereticornis under two different pulping conditions.

EXPERIMENTAL

Raw material preparation

The logs of 5 year old Eucalyptus tereticornis (first crop) were collected from the campus of Forest

Research Institute, Dehradun. The specific gravity of wood was 0.64. Middle portion of the logs were chipped in Walterous four knife pilot plant chipper of Cellulose and Paper Division, FRI, screened and stored in polythene bags for further experiments. Chips had 13% moisture content.

Pulping

Wood chips (25x15x2-3mm) were pulped in air pulping bath unit using 12,14,16 and 18% active alkali as Na₂O. Sulphidity 25%, bath ratio 1:4 and maximum temperature, 165°C were kept constant in all the cases. Room temperature to 100°C temperature was raised in 30 minutes followed by 10°C rise in 15 minutes up to 160°C. 160°C to 165°C temperature was raised in 5 minutes. At 165°C pulping was carried out for 60 minutes. Pulping schedule corresponds to H-factor, 810. The cooked material was washed with hot water, fiberized in laboratory disintegrator and screened over flat laboratory screen having 0.25 mm slots. Pulp yield and kappa number were determined in each case.

Beating sheet making and physical strength properties

Unbleached pulps were beaten in PFI mill at different revolutions. Hand sheets of 65±2% gsm of each pulp, were made on standard British sheet making machine equipped with water circulation system, air dried,

conditioned at $27 \pm 1^\circ\text{C}$ and $65 \pm 2\%$ relative humidity and tested for various strength properties. Results were interpolated at freeness 250 (ml) csf.

Isolation and purification of lignins

Extractive free, air-dried dust (40-60 mesh) of *E. tereticornis* wood and its kraft pulps of two different kappa numbers were refluxed with acidified solvent (dioxane-water 9:1 v/v, acidified with hydrochloric acid equivalent to 0.2N normality) for 48 hours under nitrogen atmosphere and allowed to cool. The dust was filtered off and the solvent mixture was concentrated under reduced pressure at $45-50^\circ\text{C}$ till a gummy material containing crude lignin appeared. The gummy material was added to large volume of vigorously stirred water, coagulated lignin was separated by centrifugation and decantation and washed thoroughly with water three times by centrifugation (1). Purified lignin was dried in a vacuum dessicator under reduced pressure over anhydrous sodium sulphate.

Elemental composition of lignin

Perkin-Elmer automatic elemental analyzer was used for determination of carbon and hydrogen and oxygen was calculated by difference.

Functional groups analysis

Methoxyl groups were determined by adopting TAPPI standard method, T-209-OS-72. Total hydroxyl, phenolic hydroxyl, carbonyl and carboxyl groups were determined by acetylation method, UV spectrophotometric method (2), hydroxylamine hydrochloric method (3) potentiometric titration method (4) respectively.

Infra-red spectroscopy

Perkin-Elmer IR Spectrophotometer model - 735 was used for IR spectroscopy. IR spectra were recorded in range of 400 cm^{-1} to 400 cm^{-1} in potassium bromide pellets. The peak area of different absorption bands were calculated. Relative peak area was calculated by dividing the individual peak area by that of peak area of 1500 cm^{-1} .

Alkaline nitrobenzene oxidation of lignin

Alkaline nitrobenzene oxidation of lignin was carried out in stainless steel bombs (5) under following conditions.

Lignin, g	0.1
Nitrobenzene, ml	0.8
Sodium hydroxide (2N), ml	6.0
Maximum temp, $^\circ\text{C}$	170
Time, min.	
Time to raise the temp. to 170°C	60
Time at 170°C	90

Purification of nitrobenzene oxidation products

From the cooled oxidation mixture, unused nitrobenzene and its reduced products were extracted with diethyl ether (5x20 ml) and discarded. Remaining aqueous solution was acidified to $\text{pH} \approx 2$ with hydrochloric acid (5 N) and oxidation products were extracted with dichloromethane (4x50 ml) and diethyl ether (4x50 ml). Both the solvent fractions were mixed together. Combined solvent fraction was dried over anhydrous sodium sulphate, reduced to small volume in a rotary evaporator under reduced pressure, transferred to a dry vial and again reduced to near dryness (≈ 0.4 ml) under nitrogen atmosphere.

Characterization of nitrobenzene oxidation products

Perkin - Elmer (USA) model - 235 High Performance Liquid Chromatograph (HPLC) equipped with programmable LC binary pump and UV diode array detector model -235 was used to characterise the alkaline nitrobenzene oxidation products. Eight compounds were identified by comparing the retention time with that of authentic samples and observing the peak enhancement on adding respective authentic sample to the oxidation mixture. Chromatography was performed under following conditions:

Column	Reverse phase pectophere sphere C_{18} column having 12% loading of bonded monomer
Elution media	0.5 N acetic acid and acetonitrile (85:15 v/v)
Elution rate, ml/min	0.5
Scanning wave length, nm	280
Peak width, nm	25
Band width, nm	8
Chart speed, mm/minute	10

Quantitative estimation of oxidation products

Known amount of each identified oxidation product was mixed together and dissolved in the solvent mixture used for the HPLC analysis. Stock solution was diluted to five different concentrations and chromatographed under identical conditions of analysis matching to the analysis conditions of oxidation products. Peak area for each compound at different known amount was calculated, calibration graphs were made by plotting the peak area against the amount of compound injected for analysis and a constant was derived in each case. The amount of each compound

Table 1. Pulping conditions, pulp yield and kappa number of *E. tereticornis* kraft pulps

Particulars	Kraft pulps of <i>E. tereticornis</i>			
	12	14	16	18
Active alkali as Na ₂ O, %	12	14	16	18
Kappa number	56.34	44.91	32.69	26.46
Total pulp yield, %	52.52	50.30	46.57	46.10
Screened pulp yield*, %	44.70	49.70	46.40	46.00

in the oxidation mixture was calculated by multiplying the peak area with the constant derived for respective compound. From these data relative percentage, relative moles and relative molar ratio were computed.

RESULTS AND DISCUSSION

Effect of alkali charge on pulp yield, kappa number and strength properties of unbleached pulps

It is observed that under identical conditions of pulping, pulp yield and kappa number decreased with the increase in alkali charge, as expected Table-1 Screened pulp yield was 44.70, 49.70, 46.50 and 46.00% for 12, 14, 16 and 18% alkali charge, respectively corresponding to 56.34, 44.901, 32.69 and 26.46 kappa number.

Burst index (kPam/g), 4.43 and 4.84, tensile index (Nm/g), 67.00 and 72.00, tear index (mNm/g), 8.40 and 8.20 at freeness 250 (ml) csf were exhibited by pulp produced using 14 and 18% alkali (Table 2). Marginally superior bonding properties for pulp produced using 18% as compared to 14% alkali may be attributed to more flexible/collapsible fibres obtained

at higher alkali charge while marginally higher tear index for pulp produced using 14% alkali may be attributed to slightly more stiffer and less collapsible fibre due to comparatively higher amount of residual lignin in pulp as compared to pulp produced using 18% alkali. Above assumptions are also in agreement with the lower degree of delignification at lower alkali charge (Table 2).

Elemental composition and functional groups of lignin from wood and pulps of *E.tereticornis*

Results recorded for elemental composition revealed that the wood lignin contains carbon (58.20%), hydrogen (6.20%) and oxygen 35.60%), while the pulps lignin of kappa number 44.91 and 26.46 contain 60.35% and 61.85% carbon, 5.95% and 5.60 hydrogen and 33.70% and 32.55% oxygen, respectively (Table 3.) Lower amount of carbon and higher amount of hydrogen and oxygen in wood lignin as compared to pulps lignin may be due to presence of comparatively higher amount of polysaccharides fraction linked with lignin via fairly stable covalent bonds (6) commonly known as Lignin Carbohydrate Complexes (LCC). However, these LCC bonds might have cleaved under alkaline conditions at elevated temperature during

Table 2. Physical strength properties of unbleached *E.tereticornis* kraft pulps at freeness 250ml (CSF)

Alkali charge, *	Aparent Density,	Burst index,	Tensile index,	Tear index,
%	g/cm ³	Kpam ² /g	Nm/g	mNm ² /g
14	0.71	4.43	67.00	8.40
18	0.72	4.84	72.00	8.20

Percentage based on o.d. raw material

Table 3. Elemental composition of wood and pulps lignin of *E.tereticornis*

Particulars	unit	Wood lignin	Pulp lignin, Kappa number 44.91	pulp lignin Kappa number 26.46
Carbon	%	58.20	60.35	61.85
Hydrogen	%	6.20	5.95	5.60
Oxygen	%	35.60	33.70	32.55

Table 4. Empirical formula of dioxane lignin of wood and pulps of *E.tereticornis*

Particular	Wood lignin	Pulp lignin, Kappa number 44.91	Pulp lignin Kappa number 26.46
Carbon	9	9	9
Hydrogen	9.311	7.924	6.937
Oxygen	2.248	1.945	1.861
Methoxyl group	1.415	1.351	1.303
Alcoholic hydroxyl group	1.708	1.291	1.186
Phenolic hydroxyl group	0.181	0.163	0.127
Carboxylic group	0.045	0.067	0.075
Carboxyl group	0.030	0.042	0.073
Molecular mass	228.52	218.29	212.29

Table 5. Ratio of the various band intensities of IR spectra of dioxane lignin of wood and pulps of *E.tereticornis*

Particular	Wood lignin	Pulp lignin, Kappa number 44.91	Pulp lignin Kappa number 26.46
1270 ⁻¹ /1230cm ⁻¹	0.8572	0.1364	0.1515
1020 ⁻¹ /1130cm ⁻¹	0.2270	0.0700	0.0500
1330 ⁻¹ /1500cm ⁻¹	0.3270	0.3800	0.3400

pulping leading to increasing the ratio of aromatic nuclei in pulps lignin, consequently, resulting into increase in carbon content in pulps lignin.

Further, it was also observed under comparatively severe conditions of pulping i.e. at kappa number 26.46 as against 44.91, increase in carbon content and decrease in hydrogen and oxygen content was more pronounced. It may again be attributed to higher amount of cleavage of LCC bonds under severe conditions of pulping. Similar is the trend in the empirical formula of the lignins (Table 4).

Methoxyl content per C₆ unit for wood lignin and pulps lignin of kappa number 44.91 and 26.46 was 1.415·1.351 and 1.303, respectively (Table 4). The decrease in methoxyl group in pulp may be attributed to the demethoxylation of methoxyl groups and easy cleavage of syringyl unit during pulping leading to decrease in syringyl unit in pulp lignin, consequently the methoxyl content (7). A slight drop in methoxyl content in the pulp lignin isolated from the pulp of kappa number 26.46 over lignin isolated from the pulp of kappa number of 44.91 may be attributed to slightly higher demethylation and more degradation of syringyl units under comparatively severe condition of pulping, however, it was still higher than the wood lignin. It is in agreement with studies carried out by other group of researcher (8).

The higher methoxyl value of wood lignin in comparison to pulp lignin was also in agreement with IR spectroscopic studies (Table 5 and Fig. 1) as the ratio of absorption intensities at 1270cm⁻¹/1230 cm⁻¹ and 1020cm⁻¹/1130cm⁻¹ were lower and intensity

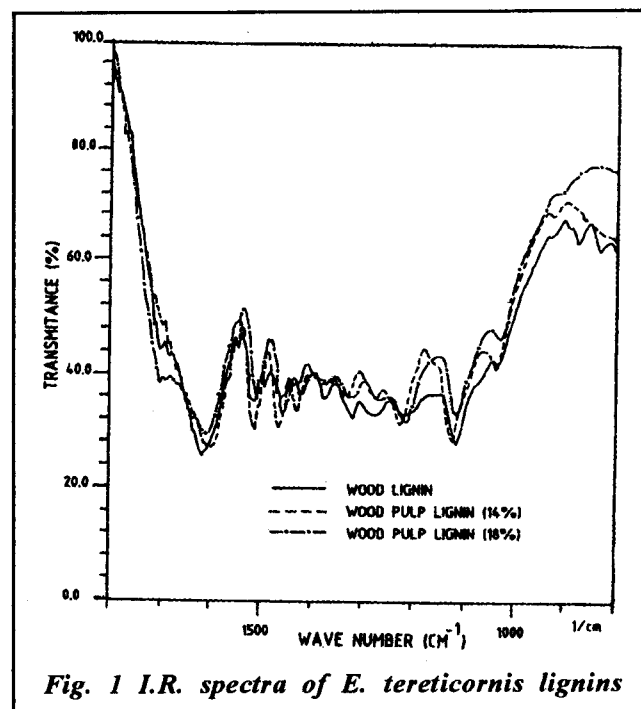


Fig. 1 I.R. spectra of *E. tereticornis* lignins

Table 6. Relative retention time, percentage, relative moles and relative molar ratio of alkaline nitrobenzene oxidation products of wood and pulps lignin of *E.tereticornis*

Oxidation products	RRT *min	Wood lignin			Pulp lignin kappa number 44.91			pulp lignin kappa number 26.46		
		RP*	RM*	RMR*	RP*	RM*	RMR*	RP*	RM*	RMR*
p-hydroxy benzoic acid	0.65	26.62	0.190	31.31	25.09	0.182	28.30	22.28	0.165	25.69
Vanillic acid	0.72	2998	0.179	29.06	13.87	0.083	12.92	12.86	0.077	11.98
Syringic acid	0.75	24.957	0.126	20.455	14.38	0.073	11.36	14.59	0.074	11.52
p-hydroxy benzaldehyde	0.845	4.224	0.0346	5.617	12.64	0.1036	16.13	12.53	0.012	15.99
Vanillin	1.00	3.419	0.023	3.734	10.80	0.071	11.05	10.66	0.070	10.89
Syringaldehyde	1.12	8.407	0.046	7.468	8.74	0.048	7.47	10.95	0.060	9.34
Aceto Vanillone	1.18	2.389	0.014	2.273	9.05	0.054	8.41	9.79	0.059	9.19
Aceto syringone	1.30	-	Traces	Traces	5.41	0.028	4.36	6.330	0.035	5.45

*RRT=Relative retention time, RP=Relative percentage, RM=Relative moles and RMR=Relative molar Ratio

at 1330cm⁻¹/1500cm⁻¹ was higher in pulps lignin to that of wood lignin (9). Thus on pulping, the residual lignin in pulps approaches towards soft wood lignin.

The phenolic hydroxyl group per C₉ unit for wood and pulps lignin of kappa number 44.91 and 26.46 was 0.181, 0.163 and 0.127. Decrease in phenolic hydroxyl group in pulps lignin may be attributed to the fragmentation of α-β phenyl units having free phenolic hydroxyl groups via cleavage of aryl ether linkages leading to dissolution of these fragmented units in alkaline media and leaving behind more condensed lignin macro molecule (10). Carboxylic group was increased from 0.045 for wood lignin to 0.060 and 0.075, respectively for lignin isolated from pulps of kappa number 44.91 and 26.46. Carbonyl group was 0.030 in wood lignin and increased to

0.042 and 0.073 for the lignin isolated from pulps corresponding to kappa number 44.91 and 26.46. These carbonyl groups might have formed during the course of alkaline delignification and also contribute to the darkening of lignin/pulp as these are conjugated to the aromatic nuclei (11,12).

Alkaline nitrobenzene oxidation products of wood and pulps lignin *E.tereticornis*

Relative percentage and relative moles of nitrobenzene oxidation products of wood and pulps lignin revealed that the formation of aldehydes increased, considerably, in pulp lignin over wood lignin, while the formation of acids decreased. The relative moles of vanillin: syringaldehyde: p-hydroxy benzaldehyde for wood lignin was 3.734 : 7.47: 5.617 and increased

Table 7. Total Relative ratio of alkaline nitrobenzene oxidation products of wood and pulps lignin of *E.tereticornis*

Particular	Wood lignin	Pulp lignin, Kappa number 44.91	Pulp lignin Kappa number 26.46
Guaiacyl	1.256	1.40	1.22
Syringly	1.00	1.00	1.00
p-hydroxy phenyl	1.32	1.92	1.58
Vanillin	0.50	1.48	1.17
Syringaldehyde	1.00	1.00	1.00
p-hydroxy benzaldehyde	0.75	2.16	1.72

to 11.05: 7.47: 16:13 and 10.89: 9.34: 15.99, respectively in pulp lignin of kappa number 44.91 and 26.46, respectively (Table 6). The improvement in the relative moles of aldehydes in pulps lignin may be due to the formation of higher amount of double bonds conjugated with phenyl nuclei (13,14) and presence of higher amount of carbonyl group. In the aromatic nuclei possessing free phenolic hydroxyl group at p-position, delocalize its dipole and the electron with drawing nature of >C=O group prohibits electron transfer through quinone methide unit with the formation of enol structure and finally breaking down to aldehydes (15). Quantitatively, the relative molar ratio of vanillic acid: syringic acid: p-hydroxy benzoic acid in wood lignin was 29.06: 20.455 : 31.31 and decreased to 12.92: 11.36: 28.30 and 11.98 : 11.529 : 25.69 in pulps lignin isolated from pulps of kappa number 44.91 and 26.46, respectively (Table 6).

The molar ratio of the aldehydes was 0.50 : 1.00 : 0.75 for vanillin: syringaldehyde: p-hydroxy benzaldehyde in wood lignin and 1.48 : 1.00 : 2.16 and 1.17 : 1.00:1.72 for pulps lignin of kappa number 44.91 and 26.46, respectively (Table 7). The ratio of total guaiacyl unit : total of syringyl unit : total of p-hydroxy phenyl unit was 1.256 : 1.00: 1.32 for wood lignin as against 1.40 : 1.00 : 1.92 and 1.22: 1.00 : 1.58 for pulps lignin of kappa number of 44.91 and 26.46, respectively (Table 7). These values indicated that perhaps during the course of delignification, the syringyl units suffered more degradation than the other two units (7). This is also in agreement with the lower methoxyl group in pulps lignin as compared in wood lignin (Table 4).

CONCLUSION

Elemental composition studies of dioxan lignins isolated from *E. tereticornis* wood and its pulps of 44.91 and 26.46 kappa number revealed that the carbon content in pulps lignin was higher than of wood lignin, while the oxygen and hydrogen content was lower. Methoxyl content, alcoholic and phenolic hydroxyl groups decreased while the carbonyl and carboxyl groups were increased in pulps lignin as compared to wood lignin. IR spectroscopic studies of lignin samples also indicated the decrease in methoxyl content in pulps lignin. Eight compounds, namely p-hydroxy benzoic acid, Vanillic acid, Syringic acid, p-hydroxy benzaldehyde, vanillin, syringaldehyde,

acetovanillone and aceto syringone were identified in alkaline nitrobenzene oxidative products by HPLC qualitatively. It was observed that the relative yield of aldehydes was increased while the relative yield of acids decreased. The lower molar ratio of syringaldehyde to vanillin and p-hydroxy benzaldehyde and also total syringyl units to total guaiacyl and p-hydroxy benzyl units indicated that syringyl units suffered more degradation during pulping than that of the guaiacyl and p-hydroxy benzyl units, consequently, the residual lignin in pulps was more nearer to soft wood lignin as compared to wood lignin.

REFERENCES

1. Pepper, J.M.; Baylis P.E.T. and Alder, E., *Can. J. Chem.*, 37, 1241 (1959).
2. Aulin - Erdtman, G.; Bjorkman, A. : Erdtman, H. and Haggbluna, S.E. *Svensk Papperstidn*, 50, 81 (1947).
3. Gierer, J. and Sodenberg, *SActa chem. Scand*, 13, 127, (1959).
4. Samuelson, O. and Tornell, B, *Svensk Papperstid*, 64, 155-198 (1961).
5. Gee, M.S.; Nelson, O.E. and Kuc, J, *Arch. Biochem. Biophys*, 123, 403 (1968).
6. Bjorkman, A. and Person, B., *Svensk Papperstidn*, 60, 158, (1957).
7. Chiang, V.L. and Funaoka, M., *Holzforchung*, 44, 214, (1990).
8. Ball, F.J. Puschel, R., *U.S. Patent 2976*, 273 (1961).
9. Sarkanen, K.V.; Chang, H.M. and Allan, G.G., *Tappi J.*, 05, 583, (1967).
10. Gierer, J. Lenz, B. Boreen, I and Sodenberg, S., *Tappi J.*, 47, 233, (1964).
11. Mikawa, H. Sato, O. Takasaki, C. and Ebisawa K., *Bull. Chem. Soc. Japan*, 29, 265 (1956).
12. Wallace, T.J. and Schriesheim, A., *Tetrahedron*, 21, 227 (1965).
13. Battersby, A.R. and Greenock, I.A., *J. Am. Chem. Soc.* 83, 2592, (1961)
14. Adler, E.; Falkehag, S.I; Marton, J and Halvarson, H., *Act. Chem. Scand.*, 18, 1313 (1964).
15. Sarkanen, K.V; Chang, H.M. *Lignin : Occurrence, formation, structure reaction*, 50, 583, (1967).