na provinské felovati narod narod narod na se je na stře na čestní se střetní střetní se střední se střední se s na mení se střední produkter provinské střední se střední se střední se střední se střední se střední se střední

1 - 1 - 1 - 1 - 1 - 1 - 1 4. Haw of the parts the book include

The second s

hen i 🖡

ndia team) sifetata t Infrared studies on milled wood lignin of Eta-Reed (Ochlandra Travancorica)

Westman gree to and the set

KAPOOR* S. K., GUHA** S. R. D.

eter tessañe et se statue

ale di

10% h_{10}

- Q.S

 \sim

1.11

AL HARD MAN AND ADD THE AND AND SUMMARY all is a

Woods contain substantial amount of lignin, a natural polymer: as one of the major constituents. The chemical method of pulp making for paper manufacture from woody material involves the separation of lignin from cellulosic fibres by treating wood chips with appropriate chemicals. The variation in chemical nature of lignin present in different types of woods necessitates optimization of pulping process parameters for individual wood species. The chemical characterisation of lignin is therefore important from application point of view. from application point of view

Inspite of the complex nature of lignin macro-molecule, the infra-red spectrum of milled wood lignin (MWL) of eta-reed (*Ochlandra-travancorica*) which is a very good raw material for paper making, showed the presence of quite a few characteristic absorption bands. In addition to the usual O-H, C-H & carbonyl group frequencies the position & relativa intensities of aromatic skeletal absorption bands in 1605 to 350 cm-1 and lower region revealed that the MWL of eta-reed was composed of p-hydroxyp henyl-propane guaiacyl and stringyl units. A comparative study of the ratio of the absorbance values of major absorbancebands and that of 1500 cm-1 band for lignins isolated from different wood species Indicated the possibility of identifying the broad chemical differences in softwood, hardwood and grass (bamboo, reeds etc) lignins. chemical differences in softwood, hardwood and grass (bamboo, reeds etc) lignins.

IN FRODUCTION:

Plant tissues contain an amorphous polymeric material called lignin. Lignin is aromatic in nature and probably the most complex and least well characterized group of substances. In wood, the lignin is concentrated between and in the outer layers of fibres. It gives the wood structural rigidity by stiff ening and holding the fibres together. Wood tissues contain 18 to 38 percent lignin.

The chemical process of pulp making for paper manufacture from woody material involves the separation of lignin from cellulosic fibres by treating wood chips with appropriate chemicals. The. chemical nature of lignin is different in grasses, softwoods and hardwoods ...which are conventional raw materials for paper making. Further variation is conserved from species to species The correct knowledge of chemical character of lignin helps in proper selection & optimization of process parameters in paper making. Milled Wood lignin (MWL) which closely resembles to protolignin is preferred for characterisation studies over other forms of lig-

nin. Infra-red spectrophotometry as compared to chemical methods provides much faster and reasonably reliable method of lignin characterisation.

were aimed at The present investigations elucidating the chemical character(by identifying various functional groups) of MWL isolated from etareed (Ochlandra-travancorica) which has been proved to be a very good raw material for chemical pulping.

EXPERIMENTAL:

Milled wood lignin in powder form was isolated from the finely ground dry wood according to the method of Bjorkman¹. The infrared spectra in the range 4000-400 cm⁻¹were recorded in potassium bromide pellets on a Perkin Elmer I R. spectrophotometer model 735.

- *Senior Scientific Officer, Central putp and Paper Research Ir stitute, Dehra Dun,
- **Visiting Professor, Institute of Paper Technology, Roorkee University Saharanpur.
 - This Paper was Presented at National Contereince on Vibrational Spectoroscopy' MIT Modras, 16-18 May 1983.

TPPTA Vol. 21, No. 3 Sept., 1984

RESULTS & DISCUSSION:

In the past, efforts had been made by several lignin chemists to establish assignments of the characteristic absorption $bands^{2-9}$. Many of these assignments especially in the region 1400–1000cm⁻¹ where various aromatic ring Vibration modes and C-O stretching modes occur are stil open to doubt¹⁰.

The aromatic nuclei in the lignin represenn mainly 1,2,4-tri and 1,2,3,5-tetra substitution patterns. Many of the planer vibration modes, which are normally inactive in benzene become strongly active in aromatic molecules with polar substituents¹¹⁻¹⁴. The difficulty in correctly assigning the absorption bands associated with such vibrational modes is due to coupling effects which are unpredictable and complex and result in band shifting and splitting. There are additial bands due to carbohydrate contamination of MWL which further complicates the spectrum. An attempt to assign the various bands in the MWL spectrum of etareed in the range 4000 to 400 cm⁻¹ Fig. 1, has been made in the following lines.

3700-3000 cm⁻¹ **band**- This absorption band is common to almost all types of lignins and is due to hydroxyl groups O-H stretching frequencies both phenolic and alcoholic¹⁵-1⁷. The band is broadened due to hydrogen bonding. 3100-2800 cm⁻¹ region—Comparatively stronger band at 2950 cm⁻¹ and a shoulder at 2865 cm⁻¹ can be assigned to methyl groups. The former results from the asymmetrical and the later from symmetrical stretching mode. The stretching vibrations of methylene group near 2925 and 2955 cm⁻¹ however are not observed.

1800-1610 cm-1 region : In this region of stretching frequencies of carbonyl groups, no single strong band is visible however there is a cluster of shoulders around 1735, 1715, 1685, 1650 and 1620 cm-1 which does not permit to suggest the predominance of a particular type of carbonyl group, Okabe and Kratzal¹⁸, have assigned a1735 cm-¹ band to be due to acetyl groups attached to the lignin. Kawamura & Higuchi¹⁹ h ave shown that 1735 and 1715 cm-1 bands appear in especially prominent form in monocoty ledons (grasses, bamboos, reeds etc.). The carbonyl group which is conjugated with a phenyl group (like acetophenone) absorbs at 1685 cm⁻¹. Absorption in the 1950-1960 cm⁻¹ can originate from a ketone or aryl aldehyde group. The C=C stretching vibration of aromatic conjugated trans-double bonds occur in the 1926-1608 cm ⁻¹ range. Normally it appears as a shoulder on the more intense aromatic stretching band near 1600 cm^{-1} .

1605-1595, 1515-1505, 1460-1420, cm⁻¹ band :

These bands can be assigned as aromatic



IPPTA Vol 21. No 3 Sept. 1984

skeletal bande of guaiacyl and syringyl type compounds. 1605-1595 cm⁻¹ band is relatively pure ring stretching frequency which can be strongly associated with the aromatic C-O stretching mode. In softwood lignins and unconjugated guaiacyl model compounds the intensity of the 1600 cm⁻¹ band is significantly lower than that of 1510 cm⁻¹ band, Fig. 2. In hardwood lignins, Fig-3, and unconjugated syringyl model compounds, the intensity of the two bands is approximately equal. The intensity ratio of these two bands may also be affected by the presence of p-hydroxyphenyl esters, carboxylate ions in carbohydrate impurities, moisture [band at 1625 cm⁻¹] or condensed tannin impurities, all of which tend to increase the relative intensity of the 1600 cm⁻¹ band with respect to



Fig. 2

I.R. SPECTRA - TERMINALIA TOMENTOSA (M.W.L.)



IPPTA Vol. 21, No. 3 Sept. 1984

1510 cm⁻¹ band. The absorption bands at 1510 & 1430-1425 cm⁻¹ are considered to be ring stretching modes strongly coupled with C-H in plane deformation. The intensity of the later band is sensitive to the nature of ring substitutents. The relative intensity of the 1510 cm⁻¹ rin stretching band and the band at 1460 cm⁻¹ due to C-H bonds including methoxyl groups is reversed in softwood (guaiacyl) and hardwood (syringyl) lignins.

1330, 1270, 1220, 1170, 1120, 030 cm⁻¹ bands (there may be slight error due to shift in calibration). The bands at 127 ,1220, and 1120 cm-1 are due to quaiacyl and 1330 and 1220 cm-1 due to syringyl derivatives are assigned to ring breathing with C-O stretching. Guaiacyl bands at 1120 and 1030 cm⁻¹ are assigned to aromatic C-H in plane deformation. Softwood lignins may sometimes show two bands at 1160-1150 and 1135-1130 cm⁻¹, assignable to both of the modes as described above, or a single unresolved band. Hardwood lignins, containing both guaiacyl and syringyl nuclei, show a complex mixture of bands originating from both types of A quick method for distinguishing softnuclei wood lignin from hardwood lignin would be the intensity of 1270 cm⁻¹ band is generally more than that of 1230 cm⁻¹ band and the 1030-40 cm⁻¹ band is equal or greater in intensity to 1120-35 cm⁻¹ band in softwood lignins & vice versa, for hardwood lignins.

Absorption bands below 1000 cm⁻¹: A strong absorption band at 840 cm⁻¹ with a shoulder at 815 cm⁻¹ and relatively weaker band at 855-60 cm⁻¹ are observable in Fig. 1. These bands are charac teristic of syringyl nucleus¹⁹ and are mostly found in tropical hardwood lignins. In softwood lignins two clearly resolved bands at 815 cm⁻¹ and 855cm⁻¹ characteristic of guaiacyl ring are found. Intensity of these two bands²⁰ varies in different types of ligniu products, suggestive of relative difference in the degree of substitution in the 5-position.

Below 800 cm⁻¹ there is no prominent band in the spectrum

Relationship between various absorption maxima and molecular compositions. In the above discussions, it has become clear that syringyl and guaiacyl units exhibit clearly distinguishable spectral patterns in which the frequencies associated with the substituted aromatic nuclei are responsible for the major maxima.

In order to find the possibility of determining the amounts of syringyl propanoid and guaiacyl propanoid units in hardwood lignins-Sarkanen & Co-workers²¹ tried absorbance ratio method of prominent absorption bands as compared to the absorbance value of 1500 cm-' band which has relatively constant intensity. For eliminating the effect of conjugated carbonyl and acetate groups on the infrared spectra; the lignin preparations were reduced with sodium borohydride. In the present investigations of MWL of eta-reed, as the intensity of the absorption bands corresponding to acetate groups was very weak, the spectrum was recorded without reduction similarly for comparison, spectra of MWL of other woods were also recorded under exactly identical conditions. To determine the absorbance values of various bands, base lines as shown in Fig. 1 were drawn. The transmittance values of maxima and the corresponding points on the base lines were noted & the absorbance values were computed from these two readings. The absorbance values of individual maxima were divided by that of 1500 cm⁻¹ maximum.

Absorption band intensity relationship for MWL of etareed, and those of pine, *eucalyptus tereticornis eucalyptus regnan* and *terminalia-tomnetosa* are given in table I.

ТΔ	RI	E-1	

ABSORPTION BAND INTENSITY RELATIONSHIP WHERE A=ABSORBANCE, WAVE NUMBER INDICATED AS A SUBINDEX WITH 1500 CM⁻¹ SELECTED AS INTERNAL REFRENCE

Wood species	Ai/A 1500									
	A 1500	500	1460	1420	1330	1270	1235	1170	1130	1040
Pine Eucalyptus Regnans Terminalia	0.365 1 0.245 1	.01 .78	0.47 1.19	1.97 0.98	0.08 0.83	1.11 0.43	0.76 1.10	0.56 0.59	0.90 2.18	1.03 0.89
Tomentosa Eucalyptus	0.327 1	.41	0.67	0.48	0.22	0.74	0.71	0.43	0.95	0.97
Tereticornis Ochlandra	0.063	1.65	0.95	0.61	0.52	0.75	0.92	-	1.69	0.89
Travancorica	0.349	1.91	0.90	0.72	0.44	0.74	0.80	0.65	1.40	0.84

IPPTA, Vol. 21, No. 3 Sept. 1984

The relative intensity of 1600 cm-1 band as compared to 1500 cm-1 band is 1.91 in case of etareed, for hardwood species it varies from 1.41 to 1.78. In case of pine it is1.01, which is minimum of the five species studied. Sarkanen & cowerkers²² reported it to be1.50 for Madrona (hardwood) and have 0.58 for sapwood lignin of douglas fir. They reported the relative intensity of 1600 cm-1 band was generally low in case of model compounds having guaia cyl units than those having syringly units. Almost similar behaviour is observed in case of 1460 cm⁻¹ band. In case of 1420 cm⁻¹ absorption band the reverse behaviour is observed i.e. the relative intensity in case of pine lignin is 1.97 where as for eta reed lignin it is 0.72 closer to hardwood species. A good contrast in 1335 cm-1 band is discernible in hardwood, monocotyledon and softwood lignins. This band is almost absent in pine lignin where as in the remaining woods including etareed it is well marked. The intensity ratio of 1270-75 and 1330-40 cm⁻¹ bands (as compared to that of 1500 cm⁻¹ band) which are due to uncondensed phenylpropane units, no consistent behaviours is visible in hardwood and softwood lignins, however the ratios are maximum for pine i.e. 1.11 & 1.03 respectively. The corresponding values for etareed lignin are 0.74 and 0.84. Similarly there is no well defined pattern in the intensity ratio of 1235 and 1170 cm-1 absorption bands. The intensity ratio of 1120-30 cm-1 band is minimum in case of pine lignin, the same value being 1.40 for etareed. It appears that three clearly distinguishable patterns can easely be recognized in the spectra of MWL, namelp those belonging to uncondensed guaiacyl, condensed guaicyl and syringyl types-

CONCLUSIONS:

- Etareed MWL contains both phenolic and aliphatic hydroxyl groups which appear to be strongly hydrogen bonded.
- Presence of appereciable amount of methoxyl groups is supported by t'e absorption bands at 2950 and 2855 cm⁻¹.
- Weak shoulders between 1790 and 1605 cm⁻¹ are indicative of the presence of carbonyl groups shoulder at 1685 cm⁻¹ is likely to be due to carbonyl groups conjugated with phenyl group.
- Presence of guaiacyl and syringyl groups is confirmed by the absorption bands at 1595,1505, 1460,1420 and 1370 cm⁻¹ Greater intensity of 1595 cm⁻¹ band as compared to that of 1500 cm⁻¹ supports the presence of p-hydroxyphenyl units.
- Absorption band at 835 cm⁻¹ accompanied by shoulders at 860 & 815 cm⁻¹ is characteristic of syringyl units generally found in tropical hardwood lignins.

- Relatively greater intensity ratio of 1460 cm⁻¹ and 1510 cm⁻¹ band suggests that the etareed MWL is different to softwood lignins.
- Greater intensity of 1130 cm⁻¹ band than that of 1030 cm⁻¹ band indicates the etareed lignin to have some similarity to hardwood lignins.
- The ratio of absorbance values of 1330 cm-¹ and 1500 cm-¹ for eta-reed lignin is also more closer to hardwood lignins suggesting the presence of appreciable amount of syringyl units.

REFERENCES :

- 1. Bjorkman, A., Sversk Fejerstid., 59, 477 (1956).
- 2. Hergert, H.J., J Org. Chem., 25, 405 (1960)
- 3. Sundholm, F., Soc. Scient. Fennica. Physico-Math, XXXII (1965).
- 4. Jones, E.J., Tappi, 32 (4), 167 (1949)
- 5. Kolboe, S., and Ellefsen, O., *Tappi*, 45 (2), 163 (1962)
- 6. Durie R.A., Lynch, B.M., and Sternbell, S., Austr J. Chem., 18, 156 (1960)
- 7. Lindberg. J J., and Kenttamaa, J., Suomen Kemisticlehti., B.32, 193 (195⁴).
- 8. Lindberg. J.J., Finska Kemists medd., 69, 11 (1960)
- 9. Bolker, H.I., and Sommerville, N.G., Pulp Paper Mag. Can., 64, 187 (1958).
- 10. Michell, A.J., watson A.J and Higgins, H.B., *Tappi*, 48 (9), 520 (1965).
- 11. Scherer, J.R, Spectrochim. Acta, 19, 601(1963)
- 12. Scherer, J.R., Spectrochim. Acta, 21, 321(1965)
- 13. Scherer, J.R., Spectrochlp. Acta, 20, 345(1964)
- 14. Scherer, J.R., and Evans, J.C., Specirochip, Acta. 19. 1739 (1963).
- 15. Hergert, H.L., J. Org. Chem., 25, 405 (1960)
- 16. Durie, R.A., Lynch, B.M., and Sternbeli, S., Aust. J. Cheni. 13, 156 (1960).
- 17. Bellamy, L.J., "Infrared Spectra of Complex Molecules" Methuen Co, London.
- 18. Okabe, J. and Kratzl, K., Tappi, 48, (7) 347 (1967)
- 19. Kawamura, I. and Higuchi, T., "Chimie et Biochimie de la lignin de la cellulose et des Hemicellulose" University of Grenoble, (1964), P. 439.
- 20. Kawamura, I, and Higuchi, T., J. Japan Wood Res. Soc. 10, 200 (1964).
- 21. Hergert, H.J., J. Org. Chem., 25, 405 (1960)
- 22. Sarkanen, K. V., Chang, H. M., and Allan, G.G., *Toppi*, 50, (12), 590 (1967).
- Sarkanen, K.V., Chang, H.M. and Allan G. G., *Tappi*, 50 (12), 583 (1967).

IPPTA Vol 21, No 3 Sept 1984