

Studies on the Chemistry of Thiolignin Isolated from *Eucalyptus Grandis*

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Introduction

Although the sulphate pulping process has been in practice for more than three quarters of a century, the chemical reactions involved are still not completely known. The studies on the properties of thiolignin and commercial lignins have been carried out keeping two aspects in view viz. (i) studies on the properties of thiolignin and (ii) the reaction mechanism of delignification during sulphate process. Both the aspects have been attacked by a number of Scientists, Klason and Segerfeldt,¹ Ahlm², Enkvist³ and Hagglund⁴. Thorough investigation on thiolignin was carried out by Ahlm². He isolated thiolignin from spruce under different cooking conditions and have found their elementary composition. Klason and Segerfeldt¹ precipitated the lignin by means of Carbon dioxide and purified it by extracting with chloroform and the lignin was analysed for its elementary composition. Enkvist³ and Hagglund⁴ put forward a hypo-

Thiolignins were isolated by the acidification of the black liquors of the sulphate digestion carried out under varying degree of sulphidity and different temperatures. These thiolignins were analysed for their elementary composition. The thiolignin isolated at 25°C sulphidity was subjected to alkaline nitrobenzene oxidation. Infrared spectra of these lignins were also studied. Infrared spectroscopic studies and analytical studies of isolated thiolignins revealed that the Eucalyptus grandis thiolignin isolated under varying sulphidities of the cooking liquor are similar to each other. The structure of thiolignin is compared of guaiacyl and syringyl repeating units.

thesis for the role of sulphidity in the sulphate cooks. So far the main raw materials of study were coniferous woods. As far as Indian fibrous raw materials (chiefly hardwoods) are concerned no systematic data are available. In this investigation studies have been carried out on the properties of thiolignin obtained from *Eucalyptus grandis*.

DISCUSSION

Influence of Sulphidity

From Tables I and II it is clear that pulping of material in presence of sodium sulphite introduces sulphur into the lignin molecule. Higher concentration of sodium sulphide results in an increase in the amount of sulphur in the isolated lignin. Klason content of the isolated lignin remains practically the same upto 25 percent sulphidity. It is seen from Table I that Klason

lignin content of the pulp first decreases and then increases with the increasing sulphidity. It is also observed (Fig. 2) that the maximum lignin from the original raw material is extractable at the sulphidity of 25 percent leaving the minimum amount of the lignin (4.1%) in pulp, beyond this sulphidity the Klason lignin in pulp increases with increasing sulphidity. The increase in the lignin content of the pulp is due to the fact that at higher sulphidities, the thiolignin condenses on the pulp. The methoxyl content of all the isolated thiolignins is practically constant and is approximately the same.

Influence of temperature in sodium sulphide cooks.

From the Table II, it is clear that as the temperature increases, the lignin recovery from the black liquor increases, but the

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Table-I
Cooking, conditions for preparation of thiolignin from *Eucalyptus grandis* and analysis of Thiolignin

Total Chemicals — 20%
Temperature — 162°C
Cooking period — 4 hours (this includes 1.5 hours to reach to maximum temp.)
Bath ratio — 1:4

Sl. No.	Sulphidity %	Unbleached Pulp yield %	Sulphur in Thiolignin %	K. Lignin in Thiolignin %	Methoxyl in lignin %	Carbon in lignin %	Hydrogen in lignin %	K. Lignin in Pulp %
1.	0.00	52.0	0.00	80.1	16.1	61.31	5.98	8.7
2.	12.5	52.1	1.64	79.6	15.7	60.84	5.90	8.5
3.	25.0	53.9	1.85	80.7	15.9	60.59	5.96	4.1
4.	33.0	52.0	2.06	78.4	15.4	58.47	5.85	6.4
5.	50.0	51.6	2.54	78.0	14.6	58.60	5.70	9.5
6.	75.0	51.0	3.20	76.8	14.3	58.68	5.90	9.7

Table-II
Elementary Composition of Thiolignins Isolated from Sodium Sulphide Cooks at Different Temperatures.

Temperature °C	Yield of lignin %	Klason lignin in Thiolignin %	Sulphur in lignin %	Methoxyl %	Carbon %	Hydrogen %
120	3.6	76.9	3.43	15.7	53.80	5.36
130	3.9	76.4	3.88	14.7	51.23	5.17
140	6.2	74.8	4.01	14.0	48.98	5.05
150	6.9	74.0	4.12	14.1	48.03	4.93
160	7.2	73.6	4.14	13.9	48.60	4.86

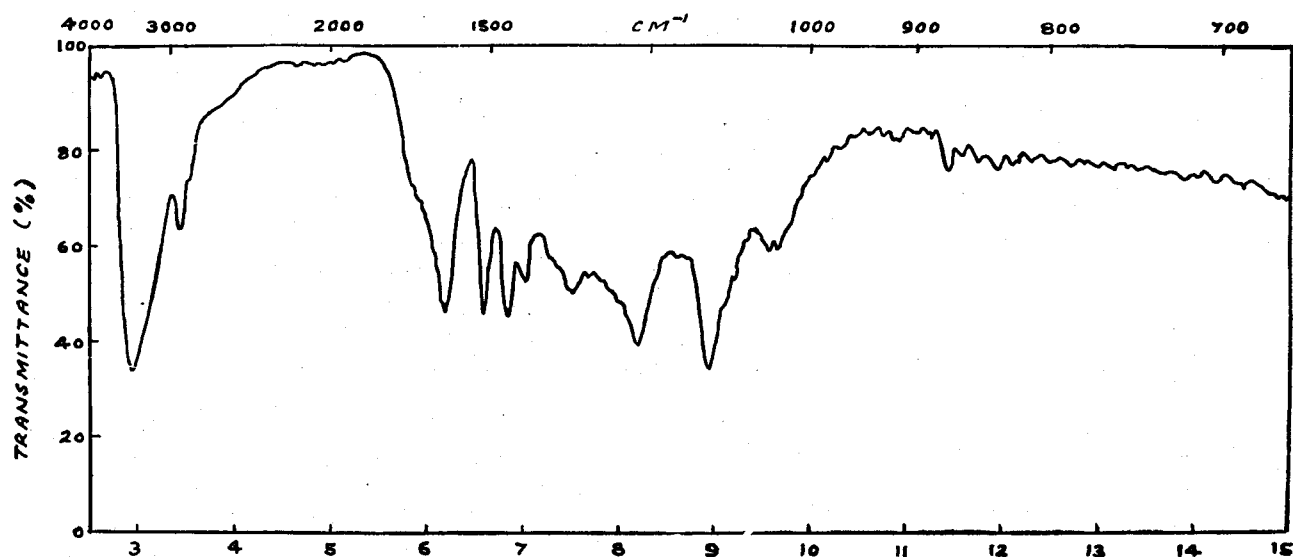


Fig. 1. Infrared Absorption Spectrum Of Thiolignin (25% Sulphidity)

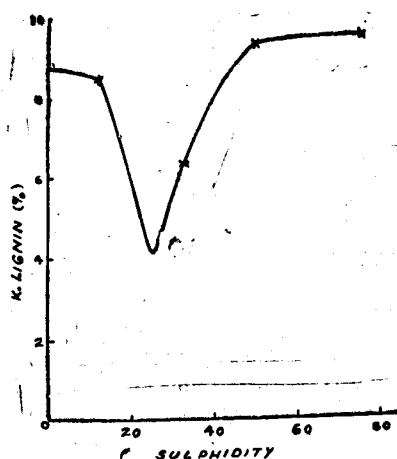


Fig. 2

carbon and hydrogen content decreases. The sulphur content in the isolated thioglignin increases with the increase of temperature and practically remains the same after the temperature of 140°C Fig. 3. This shows that even at lower temperatures there is a rapid and strong interaction between sulphur and lignin. The reaction may involve successive replacement of hydroxyl groups by hydro-sulphide ions.

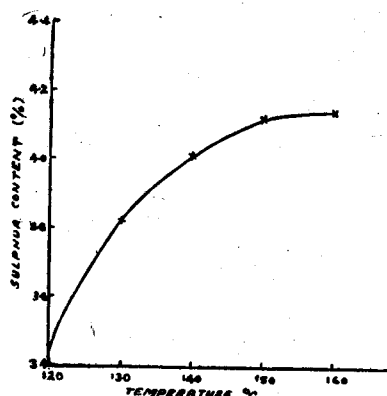
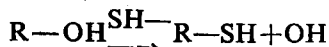


Fig. 3



Alkaline Nitrobenzene Oxidation

The alkaline nitrobenzene oxidation was carried out in case of

thioglignin obtained at 25 percent sulphidity only because in this case the maximum protolignin was dissolved out, thus giving a thioglignin which represents the major part of protolignin. vanillin (3.9%) and Syringaldehyde (6.9%) were obtained by the alkaline nitrobenzene oxidation. From this it is concluded that the structure of thioglignin is composed of syringyl and guaiacyl repeating units.

Infrared Spectra

The thioglignin isolated at 25 percent sulphidity was taken for the spectroscopic studies. In fig. 1, the bands at 3400 cm^{-1} are interpreted as arising from hydroxyl group stretching vibrations.^{5,6} Bands at 3000–2800 cm^{-1} are due to C–H stretching vibrations.⁵ In thioglignin there is no band (1700–1660 cm^{-1}) which can represent the carbonyl group. Thus principle change occurred in C=O region in case of thioglignin similar findings have been reported by Marton⁷ in the case of pine milled wood lignin (MWL) and kraft lignin. The bands at 1600–1500 cm^{-1} represent C=C skeletal vibrations of aromatic ring. The band at 1425–1420 cm^{-1} are due to the C–H bands of methoxyl group^{5,6}. The absorption at 1140 cm^{-1} is due to dialkyl ether linkages⁵.

Experimental

Sulphate digestions of *Eucalyptus grandis* were carried out by cooking 200 gm (oven-dry basis) chips in stainless steel autoclave

of 3 litre capacity at 160°C for 4 hours, the black liquors obtained were collected for the isolation of thioglignin.

Isolation of Thioglignin

Black liquors of the sulphate cooks were filtered on a muslin cloth and were taken into the glass beakers. They were heated to about 80°C and then acidified by addition of hydrochloric acid to about pH 3, to precipitate the thioglignins. These precipitates were redissolved in alkali and after filtration were reprecipitated by the addition of hydrochloric acid and were subjected to thorough washings into glass crucible funnel till free of chloride ion. These isolated lignins were purified by dissolving them in dioxane and precipitating in Petroleum ether. Similarly thioglignins were isolated at different temperatures by cooking the material with only sodium sulphide

Analysis of Thioglignin Sulphur Content

The sulphur content was determined by the Messinger Method⁸

Klason Lignin Content

Tappi Standard Method⁹ was employed for K. Lignin content determination.

Methoxyl Value

The method of Viebock and Schwappach^{10,11} was followed for the methoxyl value determination.

Alkaline Nitrobenzene Oxidation

The method of Stone and Bludell¹² was followed for the alkaline nitrobenzene oxidation of thioglignin. Oxidation products were

separated and identified by the descending method of proper chromatography using the benzene-water, solvent system. Quantitative estimation of oxidation products was also carried out.

Infrared Spectra

The infrared spectra of isolated thioglignin sample was carried out, using Perkin Elmer infracord spectrophotometer. Isolated lignin samples were examined in clear discs containing 1.8 mg. of lignin in 100 mg. of Potassium Bromide.

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