Studies on Chemistry of Pinus Caribea Lignin

Gupta Shrikant*, Madan R.N.*, Bansal M.C.*

ABSTRACT

Two types of lignins namely Thiolignin and Organosolv lignin were isolated from Pinus Carebea. Thiolignins were isolated by precipitating sulphate spent liquor with hydrochloric acid. Alcohoiic lignin was isolated by refluxing the wood meal with acidic ethyl alcohol and pourlng the extracted liquor in large amount of water. The alcoholic lignin was collected as precipitate. Isolated lignins were analysed for elemental composition methoxyl content. Oxidation of these lignins was also carried out. The chemical composition of isolated lignins corresponds to Freudinberg's general formula of lignin. These isolated lignin are mainly composed of guaiacyl propane units. Ethanol lignin seems to approach proto-lignin in comparison to thiolignin.

INTRODUCTION

Lignin is an aromatic, amorphous material which forms a part of the cell wall and middle lamella in wood. Lignin contains only carbon, hydrogen and ovygen. The constitutional model of lignin is composed of many reactive groups such as ethers of various types, primary and secondary alcoholic hydroxyl groups, carboxyl groups, methoxyl groups, ethylene linkages and aromatic sites of phenyl propanoid structures.

The major portion of lignin can be isolated by chemical reactions which solubilize either the lignin or the polysachoharide. To study the properties and chemistry of lignin it is desirable to isolate the lignin in high yields thet chemical nature of lignin remains unchanged during isolation.

No systematic work on the chemistry of lignin of *Pinus Caribea* an important raw material for future expansion for Indian Paper Mills has been done. It is desirable to work with isolated lignin preparations in studying the properties of lignin. Ideally the goal is isolation of a preparation which does not contain any non-lignin substance and which utilizes procedures sufficiently mild that the chemical nature of the lignin remains unchanged during isolation.

The organosolv lignin are the reaction products which has been obtained from the wood dust and organic solvents in the presence of an acid catalyst. Thiolignins are obtained by precipitating the spent sulphate liquor with acid.

Most of the works reported in literature on the chemistry of lignin has been done on pine occuring in Europe and North America. *Pinus caribea* is an exotic species and is being planted in the tropical countries especially to meet the demand of Pulp and Paper Industry. Therefore it will be appropriate to study the chemistry of *Pinus caribea* lignin which will give a better idea in understanding its pulping. In the present study two types of lignins namely Thiolignin is important from commercial point of view and organosolv seems to approach protolignin and it will be interesting to compare two types of lignins. For these investigation *Pinus caribea* logs were collected from the Forest Research Institute, Dehradun.

Experimental :

Preparation of extractive free dust—

Pinus caribea billets were chipped. These chips were then coverted into dust (60-80 mesh). The dust was exhaustively extracted with a mixture of one volume of 95 percent ethyl alcohol and two volumes of benzene. The extracted dust was washed with hot water.

Thio Lignin :

Pinus caribea chips (200 g) were digested by sulphate process in an autoclave using 10 percent chemi-

* Institute of Paper Technology, (U.O R.) Saharanpur-247001.

cals, keeping the bath ratio 1:4 at 162°C for 4 hours. including 1 hour to raise the temperature. From the alkaline liquor thio lignin was precipitated by hydrochloric acid. The yield was 5.2 percent on oven dry chips.

Ethanol Lignin :

Pre-extracted *Pinus caribea* dust (200 g), was taken in a 5 litre round bottom flask fitted with a reflux condenser Ethyl alcohol (3 litres) containing hydrochloric acid to give a solution of required acid concentration (0.2 N) was added to the flask. It was heated at 80°C for 2 hours. At the end of two hours, the reaction mixture was filtered and the dust was washed with ethyl alcohol. The excess of vigorously stirred water in order to precipitate the ethanol lignin. The ethanol lignin precipitate was washed thoroughly with distilled water by centrifugation and dried over phosphorous pentaoxide. The yield of ethanol lignin was 8.2 percent.

Examination of Lignin :

Composition of isolated lignins—

Elemental composition, and methoxyl content of these lignins were determined by standard methods. The results of analysis are recorded in Table—1. The analysis of total hydroxyl groups were carried out by the procedures followed whistler[1] and the results are also recorded in Table—1.

Infra-red spectra:— Perkin Elmer infra-red spectrophotometer was used. Isolated lignins were examined in clear discs containing 1.8mg of lignin in 100 mg. of potassium bromide.

Alkaline nitrobenzene oxidation :—

Alkaline nitrobenzene oxidation of isolated lignins was carried out according to the method of Stone and Blundel[2]. A sample (~5 *g*) of lignin was heated in a stainless steel bomb at 160°C for 2 hours with (7 ml) 2N caustic soda and (0.5 ml) nitrobenzene. The oxidation products were separated by Bland and Stamp[3] method. The amounts of aldehydes are recorded in Table – 2.

Results And Discussion

The yield of *Pinus caribea* Thiolognin and Ethanol lignin is 5.2 and 8.4 respectively on the basis of wood. The lower yield in Thiolignin in comparision to Ethanol lignin is due to dractic action during sulphate cooking. The colour of Thiolignin is dark brown whereas of Ethanol lignin is creamy due the reasons mentioned above.

The results of elementary composition are recorded in Table—1. From the results it is evident that carbon content is higher in case of Ethanol lignin than thiolignin. But in both cases the carbon content is higher which shows its aromatic nature. The results of chemical composition of *Pinus caribea* lignin are comparable

TABLE—1

Composition of **Pinus Caribea** Lignins

Sl. No.	Type of lignin	Carbon %	Hydrogen %	Oxygen %	Methoxyl %	Hydroxyl total %	Calculated C_9 formulae
1.	Thiolignin	60.34	6.12	33.54	13.96	9.58	$C_9H_{8.29}O_{2.15}(OCH_3)_{.88}(OH)_{1.1}$
2.	Ethanol Lignin	62.52	6.32	31.16	14.85	8.12	$C_9H_{8.30}O_{1.89}(OCH_3)_{.91}(OH)_{.90}$
3.	Spruce dioxane Lignin[4]	64.1	6.23	29.76	17.10	—	$C_9H_{8.80}O_{2.6}(OCH_3)_{.96}$

TABLE—2

Nitrobenzene Oxidation Products of **Pinus Caribea** Lignins

Sl. No.	Type of Lignin	Vanillin (V) %	Syring-aldehyde (S) %	p-hydroxy benzalde-hyd %	Total aldehydes %
1.	Thiolignin	13.10	0.86	1.62	15.58
2.	Ethanon Lignin	14.25	1.12	2.81	18 18
3.	Pine dioxane lignin[7]	20.6	Trace	1.60	22.20

to other soft wood lignin reported in literature[4,5]. The results of functional groups like methoxyl and hydroxyl recorded in Table—1 show that the values of hydroxyl are in the range of soft wood lignin 8.12-9.50%. Value of methoxyl per C_9 is 0.90 of Pinus caribea which is comparable to the values of methoxyl per C_9 from spruce lignin (0.96) shown in Table 1. Methoxyl value per C_9 in case of hard wood is generally higher (1.2-1.5) due to syringyl units present in hardwood[6]. Syringyl units are in traces in soft wood lignin. The value of hydroxyl content is higher in thiolignin in comparison to ethanol lignin which may be due the splitting of methoxyl groups of lignin to hydroxyl during pulping. The value of hydroxyl content and methoxyl content is almost same in case of ethanol lignin.

As lignin is built up of phenyl propane monomer units, therefore C_9 formula of Thio-lignin and Ethanol lignin are $C_9H_{8\cdot29}O_{2\cdot15}(OCH_3)_{\cdot88}(OH)_{1\cdot1}$ and $C_9H_{8\cdot39}O_{1\cdot89}(OCH_3)_{\cdot91}(OH)_{\cdot90}$ respectively. These C_9 formulae are comparable to other soft wood lignin reported in Table—1[7,8].

Nitrobenzene oxidation products of *Pinus caribea* lignin are recorded in Table-2. These are mainly vanillin and with very small amount of syringaldehyde and h-hydroxybenzalde. Higher percentage of vanillin shows that Pinus caribea lignin is mainly built up of guaiacyl units. Generally soft wood lignins of oxidation gives 20-25% vanillin. The yield of aldehydes in case of *Pinus caribea* is 15.38—18.18% which is comparable to pine dioxane lignin (22.2%).

Sarkanen and Ludwig[9] and Browning[10] have given in Tabular form assignment of infra-red absorption band in lignin. The band at 3375 cm^{-1} represents the presence of hydroxyl group, the band at 2830 cm^{-1} is due to methoxyl group and the band at 1270cm^{-1} represents the guaiacyl ring breathing with C=O stretching. The chemical analysis data revealing methoxyl, hydroxyl and guaiacyl units are confirmed by the spectral analysis. From the above results it can be concluded that Pinus caribea lignin is composed of mainly guaiacyl units. Ethanol lignin seems to approach protolignin in comparison to Thiolignin.

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