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Introduction

The organosolv¹ lignins are the reaction products which have been obtained from the wood dust by the organic solvents in the presence of an acid catalyst. Several lignin chemists have carried out the work on the organosolv lignins.

Klason¹ Gruss², Friedrich and Diwald³ have carried out the work on the isolation of ethanol lignin by using the different percentages of hydrochloric acid. Paper and Siddiqueullah⁴ isolated dioxane lignin from softwoods, hardwoods and straws by acidolysis in a dioxane water medium. Brauns and Buchanan⁵ isolated acetic acid lignin from spruce wood using glacial acetic acid and magnesium chloride as catalyst. Bailev⁶ prepared the butanol lignin by extracting sqruce wood with mixture of butanol and sodium hydroxode solution. Studies have shown that very little work has so far been done to

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Studies on the Chemical Constitution of Organosolv Lignin Isolated from Eucalyptus Grandis

Dioxane lignin, isobutanol lignin, acetic acid lignin and ethanol lignin at different concentrations (0.2N-1.2N) of hydrochloric acid were isolated from E. grandis. These lignins were studied with respects to their elemental composition, molecular weight determination, infrared spectrum and alkaline nitrobenzene oxidation. These studies have shown that syringyl and guaiacyl are the chief building units of E. grandis lignin and these units are distributed in a definite ratio (1.9-2.1) in E. grandis lignin. It has also been found thut syringyl repeating units are more in number as compared to guaiacyl repeating units. Metboxyl, carbonyl, aryl alkyl ether, hydroxyl groups both phenolic and alcoholic are mainly present in E. grandis lignin. The analysis of isolated lignins have shown that method of isolation and change of organic solvent does not effect the basic structure of E. grandis lignin.

study the nature of the Eucalyptus grandis lignin. This paper describes the isolation of organosolv lignin (Dioxane lignin, ethanol lignin, acetic acid lignin, and isobutanol lignin) and study of their analysis.

Discussion

Ethanol lignin: The analysis of lignin isolated by extraction of *E. grandis* dust with increasing initial concentration of hydrochloric acid in ethyl alcohol shows that the percentage of carbon increases whereas the percentage of hydrogen and methoxyl content decreases wilh increasing concentration of the acid. This may be due to an increasing extent of infra molecular dehydration.

The alkaline nitrobenzene oxidation (Table III) of ethanol lignin gives vanillin and syringaldehyde indicating the presence of syringyl and guaiacyl units. The higher vield of syringyldehyde as compared to vanillin indicates that there are more number of synringal repeating units than guaiacyl repeating units. This is also evident from the higher methoxyl value obtained in E. grandis lignin. Further it is seen that the yield of vanillin and syringaldehyde decreases as the concentration of hydrochloric acid increases in the isolation but there is no appreciable difference in the ratio of

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syringaldehyde to vanillin and it is practically the same (Table-III). This suggests that the lignin isola ted from *E. grandis* is composed of syringyl and gauiacyl repeating units and ratio of syringyl to guaiacyl units is not affected to an appreciable extent, even under the drastic condition of isolation.

Infrared spectra of ethanol lignin, Fig. 1, shows that the bands at 3430-3400 cm⁻¹ are due to the hydroxyl groups and their frequency indicates that they are quite strongly hydrogen bonded7. The absorption bands at 3100-2800 cm⁻¹ represent various types of C-H bonds'. The bands at 1600-1500 cm-1 are characteristics of aromatic compounds and are due to c=c vibrations of benzene ring ⁷,⁸. The bands in the region of 1700-1650 cm-1 are due to B-keto structure⁷. The bands at 1425-1420 cm-1 represent C-H bonds of methoxyl groups⁷,⁸. The bands at 1270 cm⁻¹ represent aryl

Table-I

Yield and elementary composition of ethanol lignin isolated , at different acid concentrations

| SI. No. | Hypochloric acid concen- tration | Yield of lignin (on o.d. dust) | K. Lig- nin | Methoxyl | Carbon | Hydro- gen |
|------------|--|---|----------------------|----------|---------------|---------------|
| | N | % | % | % | % | % |
| 1. | 0.2 | 7.3 | 89.4 | 19.7 | 60.02 | 6.20 |
| 2. | 0.4 | 7.6 | 89.2 | 19.4 | 61.66 | 6.19 |
| 3. | 0.6 | 8.1 | 8 8. 6 | 18.5 | 62.62 | 5.87 |
| 4. | 0.8 | 8.9 | 88.4 | 18.3 | 62.7 0 | 5.84 |
| 5. | 1.2 | 9.4 | 87.9 | 17.7 | 63.1 0 | 5.80 |

Table II

Ethanol lignin isolated by successive extraction of Eucalyptus grandis dust under increasing initial acid concentration

| SI. No. | HCl concen- tration | Lignin recovery (on o.d. dust) | Combined lignin recovery (on o.d. dust) | Carbon | Hydro- gen | Metho- xyi | |
|------------|------------------------|---|---|--------|---------------|---------------|--|
| | Ν | % | % | % | % | % | |
| 1. | 0.2 | 7.3 | | 60.02 | 6.20 | 19.7 | |
| 2. | 0.4 | 4.6 | 11.9 | 60.80 | 6.10 | 19.2 | |
| 3. | 0.6 | 3.8 | 15.7 | 62.10 | 5.9 0 | 18.7 | |
| 4. | 0.8 | 2.6 | 18.3 | 62.40 | 5.84 | 17.6 | |



Fig. 1-I.R Spectra of Ethanol Lignin

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alkyl ether groups⁸. Bands at 1140-1080 cm⁻¹ are assignable to dialkyl ether groups⁸.

Dioxane Lignin: The methoxyl value and Kalson lignin content of dioxane and ethanol lignin are practically the same (Table IV & I). The alkaline nitrobenzene oxidation of dioxane lignin gave vanillin and syringaldehyde as observed in case of ethanol lignin. Though the total aldehydes obtained from dioxané lignin are more than ethanol lignin but there is no appreciable difference in the syringaldehyde to vanillin ratio (S/V) (Table V and III). The infrared spectra, Fig. 2 of dioxane lignin indicates similar type of characteristic bands as observed from the spectra of ethanol lignin. The exact nature of carbonyl groups in dioxane lignin is not assignable as carbonyl band forms a shoulder on c=c band at 1600 cm⁻¹.

Acetic Acid Lignin : The Klason lignin content of acetic acid lignin

Table III

Alkaline nitrobenzene oxidation of ethanol lignin isolated at different hydrochloric acid concentrations

| SI. No. | Acid concen- tration | Yield of | Total | Syringal- | |
|------------|----------------------------|----------|----------------|----------------|-----------------------|
| | | Vanillin | Syringaldehyde | alde- hydes | dehyde to vanillin |
| | N | % | % | % | ratio (S/V) |
| 1. | 0.2 | 5.20 | 11.16 | 16.36 | 2.1 |
| 2. | 0.4 | 4.60 | 10.42 | 16.02 | 2.2 |
| 3. | 0.6 | 3.97 | 9.90 | 13.87 | 2.4 |
| 4. | 0.8 | 3.84 | 8.40 | 12.24 | 2.1 |
| 5. | 1.2 | 3.60 | 7.40 | 12.00 | 2.0 |

Table-IV

Yield and analysis of dioxane, acetic acid and isobutanol lignin

| SI. No. | lignin isolated | Lignin recovery | Klason lignin | Car- bon | Hydro- gen | Meth- oxyl | Molecular weight |
|------------|--------------------|--------------------|------------------|---------------|---------------|---------------|---------------------|
| | - | % | % | % | % | % | (Mn) |
| 1. | Dioxane | 8.3 | 89.1 | 60.5 0 | 6.38 | 19.4 | 3220 |
| 2. | Acetic | 8.9 | 83.9 | 59.94 | 6.30 | 18.1 | 2594 |
| 3. | Isobutano | 1 7.8 | 89.0 | 61.52 | 5.95 | 219.0 | 2770 |



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is lower than ethanol lignin (Table IV & I). The alkaline nitrobenzene oxidation have shown that the lower yield of aldehydes is obtainable from acetic acid lignin as compared with ethanol lignin but there is no appreciable difference in the ratio of syringaldehyde and vanillin obtained in acetic acid lignin and ethanol lignin Table V and III). The infrared spectra Fig. 3, of acetic acid lignin shows similar type of absorption curves as obtained in case of ethanol lignin and the band at 835 cm⁻¹ of trisbstituted benzene ring has also been observed from the spectra of acetic acid lignin. The molecular weight (2594) of acetic acid lignin is lower than the number average molecular weight (2820) of ethanol lignin isolated from *Eucalyptus grandis*.

Isobutanol lignin : The alkaline nitrobenzene oxidation of isobutanol lignin gave syringaldehyde vanillin in the ratio of 2.1 (Table V)



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Table V

Yield of alkaline nitrobenzene oxidation products

| Sl. | Lignin | Oxidation | Oxidation products | | |
|-----|-------------|---------------|---------------------|----------------|-----|
| No | isolated | Vanillin % | Syringaldehyde % | aldehydes % | |
| 1. | Dioxane | 6.90 | 13.60 | 20.50 | 2.0 |
| 2. | Acetic acid | 4.10 | 7.90 | 12.0 | 1.9 |
| 3. | Isobutanol | 4.30 | 9.10 | 13.40 | 2.1 |

the same (S/V) ratio was observed in case of ethanol lignin (0.2N). The infrared spectra, Fig. 4 of isobutanol lignin is similar to spectra of ethanol lignin. This shows that isobutanol lignin resembles more than ethanol lignin. Further it has also been observed that there is no appreciable difference in number average molecular weights of isobutanol lignin (2770) and ethanol lignin (2820).

The analysis of ethanol lignin, dioxane lignin, acetic acid lignin and isobutanol lignin has shown that the method of isolation and change of organic solvent does not effect the basic structure of *E. grandis* lignin. This is supported by the following findings :

(i) The same aldehydes vanillin and syringaldehyde are obtained from the isolated lignins on alkaline nitrobenzene oxidation and the ratio of syringaldehyde to vanillin is practically the same in each case as described above. (ii) The infrared spectrascopic studies have shown that more or less similar types of absorption curves are obtained from these lignins.

There is no appreciable difference

in the Klason lignin content and methoxyl value of ethanol lignin, dioxane lignin, acetic acid lignin and isobutanol lignin. This shows that these are similar in nature.

Experimental

Material: The Eucalyptus grandis logs were chipped in the pilot plant chipper of the Cellulose & Paper Branch, Dehra Dun. The chips were then converted into dust (40-60 mesh) in the laboratory disintegrator (Willey Mill). This dust was exhaustively extracted with mixture of ethanol and benzene (1:2 V/V). The extracted dust was washed with hot water and this pre-extracted dust was used for the isolation of various organosolv lignins.

Ethanol Lignin : Pre-extracted *E. grandis* dust (200 g), was taken in a 5 litre round bottom flask fitted with a refluxe condenser Ethyl alcohol (3 litres) containing hydrochloric acid to give a solution of required acid concentration (0.2N) 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

ethylalcohol. The extract was concentrated and poured over a large 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. In the similar way ethanol lignin at different concentrations (0.4 N, 0.6 N, 0.8 N and 1.2N) of hydrochloric acid was isolated, successive extraction of F. grandis dust with increasing initial concentration of hydrochloric acid was also carried out in the similar fashion.

Dioxane Lignin : The dioxane lignin was isolated from pre-extracted E. grandis dust by the method of Paper and Siddiqueullah⁴. The dust was treated with dioxane water (9:1) solvent containing 0.2N hydrochloric acid at 80°C for two hours in an inert atmosphere of nitrogen. The reaction mixture was cooled down at 35°-40°C and then filtered on a buchner funnel. The wood residue was washed with neutral dioxane water (9:1), the filtrate and washing were combined and were concentrated under reduced pressure in nitrogen atmosphere. The lignin was precipitated by the addition of concentrated extract to a large excess of vigorously stirred distilled water.

Acetic acid Lignin: The method of Brauns and Buchanan⁵ was followed for the isolation of acetic acid lignin, pre-extracted *E. grandis* dust was refluxed for ten hours

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with glacial acetic acid in the presence of small amount of magnesium chloride. Liquor obtained by the filtration, was concentrated under reduced pressure and was dissolved in dioxane. The lignin was then isolated by dropping the solution into water. This was then purified by redissolving in dioxane and precipitating it into anhydrous ether.

Isobutanol Lignin : The 40 g preextracted *E. grandis* dust was refluxed for 2 hours with isobutanol in the pressence of 50 cc g 37% hydrochloric acid. The filtered alcoholic solution was evaporated under reduced pressure, the residue was taken up in dilute sodium hydroxide and was acidified, causing isobutanol lignin⁹.

ANALYSIS

Klason Lignin Content : The Klason lignin content of isolated lignins was determined by the Tappi Standard Method¹⁰.

Methoxyl Value : The method of Viebock and Schwappach¹¹ were followed for the methoxyl value determination.

Alkaline nitrobenzene oxidation : The method of Stone and Blundell¹² was followed for the alkaline nitrobenzene oxidation of isolated lignin samples. Oxidation products were separated and identified by the descending method of paper chromatography using the solvent system benzenewater^{1:1}. The quantitative estimation of oxidation products was also carried out.

Infrared Spectra : The infrared spectra of isolated lignin samples were carried out, using Perkin Elmer infracord spectrophotometer Model No. Isolated lignin samples were examined in clear discs containing 1.8 mg. of lignin in 100 mg. of potassium bromide. Molecular weight : Number average molecular weight (Mn) was determined by vapour pressure osmometer (3028) by the method of Marton and Brady^{13:14}.

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