

Fourier Transform Infrared Studies on Lignin From Cassia Siamea and Ailanthus Excelsa

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ABSTRACT

The structural characterisation of precipitated lignin from Cassia siamea and Ailanthus excelsa was achieved by using IR spectroscopy. The proximate chemical analysis of both the genus and IR characterisation suggest the suitability of Cassia siamea and Ailanthus excelsa for paper making.

INTRODUCTION

Lignin is considered as a natural polymer which can be separated from wood and straw by the action of organic and inorganic chemicals. It is proved that lignin is made up of phenyl propane unit attached with each other with β -O-4 linkages and bearing -OH and -OCH₃ groups.

An exhaustive survey of the literature on lignin indicated that the isolation and spectroscopic investigation of lignin from Cassia siamea and Ailanthus excelsa has not been studied earlier. Ailanthus excelsa being short fibre (average fibre length 1.22 mm) admixture with long-fibred pulp may be necessary for the production of paper.

Higher percentage of lignin contents in both the genus prompts us to remove the lignin from chemical pulp by alternative treatment with relatively inexpensive, strong oxidising agents as the lignin is very strong reducing agent¹.

Geiger² had reported the behaviour of organic and inorganic chemicals with lignin rendering to the ring opening ring hydroxylation, oxidative demethylation, oxidative ring and cleavage of ether bonds.

Alkali lignin and sulphonated lignin gave rise to carbonyl and carboxylic groups, thus rendering the lignin more soluble in water and alkaline medium. As the crystallinity index (ratio of the intensity of band

absorbance at 1400 cm⁻¹ to band absorbance at 900 cm⁻¹) of alkali lignin are higher than sulphonated lignin thereby suggesting that the preferential loss of disordered regions of cellulose during pulping process.

Infrared spectroscopy has proved to be an especially useful tool in the field of lignin chemistry since it provides a rapid method of evaluating lignin disordered by different methods³.

EXPERIMENTAL

ISOLATION OF LIGNIN

Isolation of Cassia alkali lignin (CAL), Cassia organosolv lignin (COSL), Cassia sulphonated lignin (CSL) and Ailanthus alkali lignin (AAL), Ailanthus organosolv lignin (AOSL), Ailanthus sulphonated lignin (ASL) has been achieved by following the known^{4,5} and recently modified methods⁶.

Infrared spectroscopy: The infrared spectra of isolated lignins has been scanned using Nicolet (FTIR Magna 550 series II, USA) infrared spectrophotometer with KBr pellets in the region of 4000-500 cm⁻¹

RESULT AND DISCUSSION

The proximate chemical analysis of the samples

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Table-1
Proximate Chemical Analysis

Properties	Ailanthus excelsa	Cassia siamea
Solubility %		
Cold water	2.4	3.2
Hot water	2.97	7.44
1% NaOH	18.3	22.54
Extraction %		
Water	5.2	12.5
Ethanol	2	4
Benzene	2.2	2.14
Ethyl acetate	1.8	2.62
Dioxane	0.92	0.44
Ethanol-Benzene [1:2]	2.2	4.87
Moisture %	1.4	4.77
Ash %	2.9	3.06
Lignin %	40.02	39.54

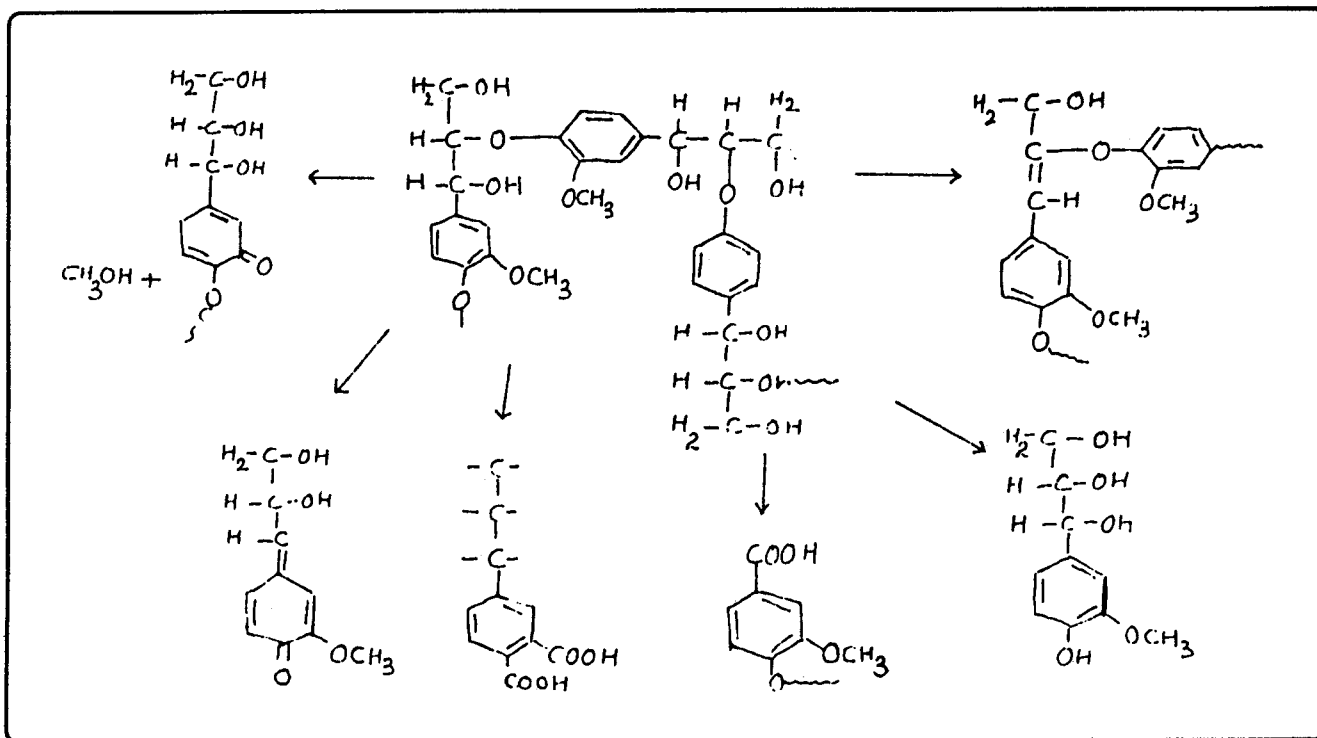
Table-2
Analysis of the FTIR absorption spectra (cm⁻¹)

CAL	COSL	CSL	AAL	AOSL	ASL
3418.77	3426.20	3458.53	3400.41	3416.61	3426.83
2935.59	2993.83	2927.31	2938.19	2923.98	2917
1725.53	1736.16	1728.77	---	1735.34	1707.36
1604.26	1630.96	1638.52	1601.04	1601.33	1622.09
1514.76	1508.86	1500.15	1514.28	1510.33	1515
1460.54	1460.33	1460	1460.71	1460.50	---
1420	1424.9	---	1424.28	1424.17	---
1328.11	1373.35	---	1375.57	1373.28	---
1267.97	1243.05	1229.47	1269.84	1266.41	---
1218	---	---	1219.54	---	1194.56
1118.84	1156.62	1125.45	1120.30	1119.5	1155.4
1025.97	1029.13	1044.97	1030.39	1034.8	1106.23
835	609.28	862.98	---	603.79	859.50

of *Cassia siamea* and *Ailanthus excelsa* were carried out to find out the different constituents of the plant biomass. The oven dried chips were powdered in pulverise mill and the powder that passed through 40 BS sieves and retained on 60 BS sieves were analysed adopting TAPPI standard methods. The results of proximate chemical analysis and IR are presented in

Table - 1 and Table - 2.

The band at 3400 cm⁻¹ is common to almost all types of lignins and is due to hydroxyl-OH stretching frequencies both to phenolic and alcoholic⁷. The band at 3400-3458 cm⁻¹ represent the presence of hydroxyl group⁸. It is observed that the bands are broadened due



Chemical reaction occurring in lignin during pulping

to hydrogen bonding in these macromolecule. The band intensity of C-O-C ether linkage at 1118, 1156, 1120, 1119 cm^{-1} of CAL, COSL, AAL, AOSL is lower than CSL and ASL. This can be confirmed by increase in C-O vibration of phenolic hydroxyl and carbonyl groups at 1375 and 1728-36 cm^{-1} respectively. This shows that sulphonated lignin has lower degrees of polymerisation than organosolv and alkali lignin.

The absorption band at 2923-2935 cm^{-1} are due to C-H vibration of CH_3 of methoxyl groups. The values of sulphonated lignin are lower than organosolv and alkali lignin suggesting demethylation.

The bands in the region of 1600-1736 cm^{-1} are do stretching frequency of various type of carbonyl groups like, α , β , keto and coniferaldehyde groups. The presence of two significant bands at 1666-1668 cm^{-1} and 1705-1710 cm^{-1} which suggest their origination from conjugated aldehyde and ketonic carbonyl groups respectively.

The bands at 1425 cm^{-1} indicated the aromatic skeletal vibration in isolated lignins. The bands at 1269.84 cm^{-1} (AAL), 1269.97 cm^{-1} (CAL), 1243.05 cm^{-1} (COSL), 1270 cm^{-1} , 1220 cm^{-1} & 1120 cm^{-1} are due to guaiacyl, and 1330 cm^{-1} and 1220 cm^{-1} are due to syringyl derivatives which can be assigned

to ring breathing with C=O stretching. It is observed that -CH band of aromatic ring at 1200 cm^{-1} is disappeared in CSL and ASL and superimposed with a band at 1269, 1200, 1243 cm^{-1} of C=O groups. This is due to degradation which has recurred in sulphite process.

The band at 1330 cm^{-1} and 1269 cm^{-1} represent two syringyl and a guaiacyl ring breathing with C=O stretching. The band at 1044 cm^{-1} (CSL) indicated the presence of dialkyl ether linkage

CONCLUSION

Alkali lignin, organosolv lignin and sulphonated lignin from *Cassia siamea* and *Ailanthus excelsa* contains both phenolic and aliphatic hydroxyl groups which appears to be strongly hydrogen bonded. Greater intensity of 1600 cm^{-1} bands as compared to that of 1500 cm^{-1} support the presence of phenylhydroxy propane units. Non availability of bands at 1420-1375 cm^{-1} (CSL, ASL) but availability at 1460 cm^{-1} (CSL) may be due to sulphonation or complex nature of lignins because no methods of it's isolation represents "Native" lignins¹⁰.

The structure and yellowing of the paper with age is depends on selectively dissolution of lignins.

The crystallinity index, proximate analysis and IR study directs the suitability of *Cassia siamea* and *Ailanthus excelsa* for paper making with or without conjunction with Bamboo species. The result of IR spectra of lignin under study also proved that the lignin are indeed essentially guaiacyl syringyl-p-hydroxy phenyl propane co-polymer though structural studies on lignin have been hampered by the random, cross-linked nature of the polymer.

ACKNOWLEDGEMENT

The authors are wish to express sincere thanks to the Director, LIT, Nagpur, for providing necessary laboratory facilities and the Director RSIC, Nagpur for scanning IR spectra. One of the author (PTK) is grateful to Principal, YCCE, Nagpur for his encouragement.

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