

Comparative Study between soda Lignin and soda Anthraquinone lignin in terms of Physiochemical Properties of Ipomoea carnea

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ABSTRACT

Non wood plants are more common as raw material where wood is scarce. In view of its easy availability of ipomoea carnea was utilized as raw material. In this study soda lignin and soda anthraquinone lignin were studied. A comparison has been made between the physico chemical properties and structural features of isolated lignin. These characterisation was done by Fourier Transform Infrared spectrometry (FTIR), Ultraviolet (UV) and High Performance Liquid chromatography (HPLC). Nitrobenzene oxidation was performed with the two types of lignin especially soda lignin and soda anthraquinone lignin. According to the FTIR report, there is no significant difference in terms of functional groups that exists in both the lignin. HPLC results however identified that in both the lignin samples the presence of vanillin and syringaldehyde was found.

Key words: Ipomoea carnea, lignin, anthraquinone, black liquor.

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INTRODUCTION

Ipomoea carnea is a common weed and locally known as *BESHARAM*. It is also known as bush morning glory which is fast growing and attains optimum size in about a year's time. Due to its high adaptability and resistance towards adverse climatic conditions, it may grow in all types of climate and soils, marshy as well as dry. A large diffused or straggling shrub with milky juice native of South America, the plant was originally used for making fence for the road side fields, but due to its massive growth and rapid propagation it has grown rapidly in barren waste lands. Plantations of ipomoea carnea may be undertaken in the month of June, July with the onset of monsoon [1].

Ipomoea carnea plant is poisonous to animals. Its leaves contain a polysaccharide-ipomus, one glucoside-anthracene a gum-gelapin and saponin. Out of the two materials, one is soluble in water and the other is in ether. Both polysaccharide and anthracene present in ipomoea carnea are water soluble poisons when enters into the central nervous system it damages the respiratory track [2], the scarcity and the restricted supply of high quality pulp and the rising price of utilities will force paper mills to adopt new technologies to conserve energy, minimum inputs, keeping environmental aspects in view, much efforts have been directed towards finding a chemical pulping process giving higher pulp yield coupled with economic and environmental considerations [3].

The process of producing cellulosic pulp from ipomoea carnea jacq requires delignification with sodium hydroxide under pressure. This process frees the cellulosic fiber from ipomoea carnea and produces a large quantity of black liquor that is discharged into surface water without effective treatment [4]. Based on the study of ipomoea carnea as lignocellulosic raw material for the pulp and paper industry, sodium hydroxide lignin extracted from soda pulping has been compared with soda anthraquinone (AQ) lignin extracted from soda AQ pulping in this study. Lignin extracted during the pulping process has so far not being investigated for its usefulness. Before its application can be considered, knowledge of its structural characterization is required; this study represents such an effort.

Lignin is an amorphous polyphenolic material arising from an enzyme mediated dehydrogenates polymerization of three major phenyl propanoid monomer which is coniferyl, sinapyl and p-coumaryl alcohol. The lignin structural elements are linked by carbon-carbon and ether bond to form tridimensional network associated with the hemicelluloses polysaccharide inside the cell wall. Lignin is usually insoluble in all solvents and can only be degraded by physical or chemical treatment. During the chemical pulping process at high temperature and high pressures degradation of lignin occurs and dissolves into the spent liquor. The delignification reactions involved the cleavage of non phenolic β -O-4 linkage, phenolic α -O-4 linkage and releasing from the associated by the polysaccharide. Addition of small quantity of anthraquinone to the alkaline pulping process increases lignin removal by promoting cleavage of interunit bonds in the lignin molecules that are not cleaved in the absence of

anthraquinone. Anthraquinone helps to minimize recondensations reactions by reacting with the carbohydrates to increase lignin removal during pulping process[5,6].

This study was conducted to characterize soda lignin and soda anthraquinone lignin in terms of their physicochemical properties and their structural features. The objective is to determine that adding anthraquinone to the pulping process changes the properties of the lignin produced. Complimentary destructive nitrobenzene oxidation and non destructive Infrared (IR), Ultraviolet (UV) and high performance liquid chromatography (HPLC) to evaluate the cross linked lignins and their linkages to cell wall polysaccharide.

MATERIAL AND METHODS

Raw material used for the laboratory experiment is ipomoea carnea jacq. The sample were collected, cleaned, chipped and screened. The screened chips were used for the experiment. About 500 gms of screened chips of ipomoea carnea jacq was pulped by soda pulping and soda anthraquinone pulping in a 20 liter stainless steel rotatory digester unit with 25% NaOH (cooking liquor) in 3hrs at a maximum cooking temperature of 170°C at a pressure of 10psi with a cooking liquor to ipomoea carnea ratio of 10:1 by weight. For soda AQ pulping 0.1% anthraquinone was added to the soda pulping system.

The soda and soda anthraquinone lignin were precipitated from the black liquor by acidifying it to pH 50mg of dry soda lignin or soda anthraquinone lignin was added to 7ml of 2M, NaOH and 0.4ml of nitrobenzene in a 15 ml steel autoclave. The autoclave was sealed tightly with a screw cap fitted with Teflon gasket and heated to 165°C for 3hrs in an oil bath. After heating the autoclave was cooled quickly by immersion in ice water. The soda lignin mixture was transferred to a liquid-liquid extractor for continuous extraction with 10ml chloroform to remove any remaining nitrobenzene reduction products and excess nitrobenzene. The oxidized mixture was acidified with conc.HCl to pH 3-4 and then extracted with 20ml chloroform. The chloroform was removed by using a rotatory evaporator at 40°C under reduced pressure to obtain nitrobenzene oxidation mixture which was used with a stock solution for further analysis.

Table-1: Yield and molar ratio of degradation products of soda lignin and soda AQ lignin by nitrobenzene oxidation

Oxidation peak	Oxidation product	Soda retention time	Liquid yield %	Soda AQ retention time	Lignin yield %
A	p-hydroxy benzoic acid(H ₁)	4.29	4.98	4.3	0.64
B	Vanillic Acid (V ₁)	5.23	3.98	5.28	5.65
C	Syringic Acid (S ₁)	5.55	4.74	5.6	4.92
D	p-hydroxy benzaldehyde(H ₂)	6.53	26.54	6.58	15.97
E	Vanillin (V ₂)	8.44	30.33	8.51	36.86
F	p-coumaric acid(B)	10.13	26.54	10.17	31.95
G	Syringaldehyde (S ₂)	12.38	2.84	12.42	3.69
Molar Ratio	S/S		1		1
	V/S		5		5
	H/S		4		2

$$S=S_1+S_2, V=V_1+V_2, H=H_1+H_2$$

Table-2: IR Stretching frequencies

S.No.	Type of Bond	Stretching frequencies	Intensity
1.	O-H Bond	3430-3400cm ⁻¹	Strong, broad
2.	C-H Bond(in methyl group)	2940-2930cm ⁻¹	Medium
3.	C-O (in carbonyl compounds)	1720-1660cm ⁻¹	Strong
4.	C-O (in conjugated carbonyl compounds with aromatic ring)	1712-1702cm ⁻¹	Medium
5.	Aromatic ring	1609-1604cm ⁻¹ 1516-1510cm ⁻¹ 1426-1422cm ⁻¹	Strong
6.	C-H Bond (bending vibrations from aromatic group)	1470-1460cm ⁻¹	Medium
7.	C-O (in syringyl group)	1330-1325cm ⁻¹ 1117-1115cm ⁻¹	Weak Medium

8.	C-O(in syringyl and guaiacyl group)	1220-1215 cm^{-1}	Strong
9.	C-O(in guaiacyl group)	1158-1155 cm^{-1} 1038-1030 cm^{-1}	Strong
10.	Bending vibrations inside aromatic plane for guaiacyl ring	1038-1030 cm^{-1}	Strong
11.	C-H deformation and ring vibration	838-834 cm^{-1}	Medium

High performance liquid chromatography (HPLC) was used to analyze the nitrobenzene mixture. Stock solution(0.25ml) was pipette into 25ml volumetric flask and made up to volume with acetonitrile:water (1:2 v/v).forty micro liter of the filtrate was injected into an HPLC system equipped with hypersil bond C_{18} column to identify oxidation product. A 1:8 mixture of acetonitrile: water containing 1% acetic acid was used as an eluent with a flow rate of 2ml min^{-1} .the eluent was monitored with an UV (ultraviolet) detector at 280nm.IR spectra were recorded with a Perkin Elmer spectrophotometer for each sample. KBr pellets were prepared containing 1% finely ground sample. For UV spectra-A Hitachi spectrophotometer was used to obtain the results. Prior to the analysis,5mg samples were dissolved in 10ml 90% (v/v) dioxane:water.The sample was then measured its absorbance for range of 210 to 350 nm.

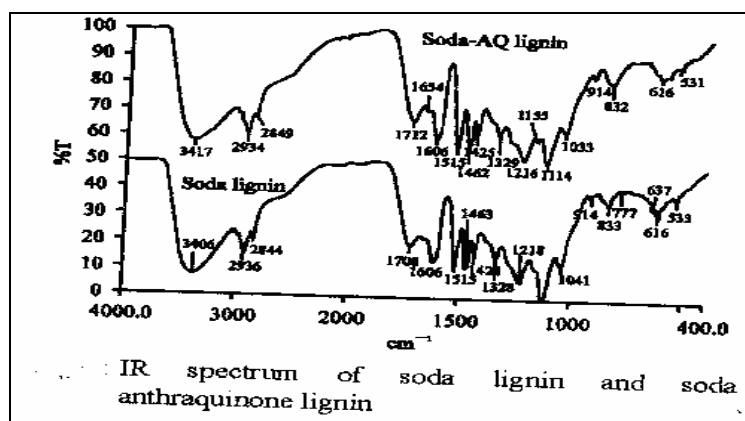


Fig.-1

RESULTS AND DISCUSSION

Yield of soda anthraquinone lignin was much higher as compared with the yield of soda lignin. It was found that anthraquinone lignin was 9.6% high than soda lignin. The amount of solubilized lignin in soda AQ black liquor is higher because anthraquinone serves as a catalyst for the soda pulping process.AQ has a marked catalytic effect on the delignification.AQ acts in a redox sequence and cycles between its oxidized and reduced forms. The oxidized AQ form reacts with quinone methide segments of the lignin polymer to increase the rate of delignification.

Nitrobenzene oxidation is one of the standard methods for analyzing lignin by chemical degradation technique in order to gain information about the composition of the original polymer. The production of aromatic aldehyde upon oxidation of lignin with alkaline nitrobenzene takes place. Three monomeric lignin units' i.e. p-hydroxyphenyl (H), guaiacyl (V) and syringyl (S) based on the amount of their degradation product. The degradation product of syringaldehyde and vanillin were analysed.Syringaldehyde was found to be predominant followed by vanillin as a second major degradation product. HPLC chromatogram for soda lignin and soda AQ lignin are similar. In general the S: V: H ratio for both syringaldehyde and vanillin. The lignin's are about the same which is 1:5:4 for soda lignin and 1:5:2 for soda AQ lignin.

IR spectra (Fig.-1) of soda lignin and soda AQ lignin precipitates have a strong and broad band at 3406 cm^{-1} which is a characteristic of OH group or phenolic compound from soda AQ lignin. The band width and strength could be due to moisture in the sample, since the OH vibration of water usually is very broad. The clear peak at 2934-2844 cm^{-1} for the soda AQ lignin is attributed to the vibration of a Methoxyl ($-\text{OCH}_3$) group while slightly different values were observed for soda lignin (2936-2844 cm^{-1}).the band at 1462 cm^{-1} is assigned to CH stretching of methyl or methylene groups and the broad medium band at 1712 cm^{-1} is due to conjugated carbonyl stretching. The three bands at 1606, 1515 and 1425 cm^{-1} are characteristics of aromatic rings due to aromatic vibrations and the band at 832 cm^{-1} indicates CH deformation and ring vibrations. The bands at 1329 cm^{-1} for soda AQ lignin and 1328 cm^{-1} for soda lignin may be due to the vibration of C aryl-O in syringyl derivatives. The bands at 1328-1329 cm^{-1} and 1216

cm^{-1} corresponds to a syringyl units and the small bands at $1033\text{-}041\text{cm}^{-1}$ are assigned to guaiacyl units of lignin molecules

CONCLUSION

Addition of anthraquinone to the pulping process does not affect the quality of lignin precipitated from soda black liquor; even though it nearly doubles the amount of lignin precipitated from black liquor. Rate of delignification was higher with 0.1% addition of anthraquinone.

The production of aromatic aldehyde upon oxidation of lignin with alkaline nitrobenzene takes place the product yielded are vanillin and syringaldehyde. Molar ratio of syringyl and guaiacyl unit varies from species to species even in the same genus and exerts its influence on rate of delignification. Higher the ratio better is the material from delignification and from processing lignin containing spent liquor points of view.

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