

## STUDIES ON THE EFFECTS OF VARIOUS MINERAL ACIDS ON THE LIGNIN PRECIPITATED FROM SODA LIQUOR OF IPOMOEAE CARNEA

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### Abstract

*Non wood plants can be used as raw material where wood is scarce. Soda lignin from ipomoea carnea was directly isolated by various mineral acids i.e. sulphuric acid, hydrochloric acid, phosphoric acid and nitric acid at three different levels of concentration. The physico chemical properties and structural features of isolated lignin were compared. Characterisation of lignin sample was carried out by Fourier Transform Infrared Spectrometry, Ultraviolet spectrometry and High Performance Liquid chromatography (HPLC). As per the FTIR report, there is no significant difference between the main structures of the lignin with the use of various acids, but low concentration of phosphoric acid is preferable as it gives highest yield. From the UV studies it was observed that phosphoric acid gave the highest absorbance value out of the four acids used in the study.*

**KEY WORDS:** *Ipomoea carnea , lignin, mineral acids ,black liquor, characterization,*

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### 1. INTRODUCTION:-

The scarcity and the restricted supply of high quality pulp and the rising price of utilities is forcing 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 which gives higher pulp yield coupled with economic and environmental considerations. Paper industry is one of the industry which is expanding rapidly to fulfill the demand of pulp and paper products but it is expected that the gap between demand and supply will increase in population growth and advancement in civilization. From the last three decade there is constant pressure to explore available non wood resources for pulp and paper making.

Available literature shows that Ipomoea Carnea Jacq stems can be used for paper making. Ipomoea Carnea Jacq grows in many parts of India. It is easy and fast growing border crop of gardens. It grows by stem transplantation throughout the year except in winter months. Due to its high adaptability and resistance towards adverse climatic conditions; it grows in all types of climate and soils, marshy as well as dry. 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.

Lignin present in wood can be considered as a random three dimensional network polymer composed of phenyl propane units which is linked together in different ways. When lignocellulosic materials are delignified, the properties of the macromolecules reflect the properties of the network Lignin is the unwanted ingredient of wood that creates most of the problems encountered during pulping. Delignification is the foremost goal of pulping. It is processed from an enzyme mediated dehydrogenates polymerization consisting of three major phenyl propanoid monomer i.e coniferyl, sinapyl and p-coumaryl alcohol. It is known as cementing material or an encrusting substance. They are formed through an enzyme catalyzed dehydrogenative polymerization. The structural elements of lignin are linked by carbon-carbon and ether bond to form tridimensional network associated with the hemicelluloses polysaccharide inside the cell wall. During the chemical pulping process at a high temperature and pressure, degradation of lignin occurs and it dissolves into the spent liquor. The delignification reactions involves the cleavage of non phenolic  $\beta$ -O-4 linkage, phenolic  $\alpha$ -O-4 linkage and is released from the associated by the polysaccharide. It contains methoxyl groups, aliphatic and phenolic hydroxyl groups

In the process of producing cellulosic pulp from ipomoea carnea jacq delignification with sodium hydroxide under pressure is required.. In this process the cellulosic fibre is made free from ipomoea carnea and it produces a large quantity of black liquor which is discharged into the surface water without effective treatment. Based on the study of ipomoea carnea as lignocellulosic raw material for pulp and paper industry and the lignin extracted from was analysed with various mineral acids. Lignin was isolated from the black liquor by various mineral acids i.e. sulphuric acids, hydrochloric acids, phosphoric acids and nitric acids at three levels of concentration (conc.,60%, and 20%).

## **2. MATERIAL AND METHODS :-**

The stalks of ipomoea Carnea of around one or two years of age was collected, cleaned, chipped & screened. Wood dust passing through 60 meshes and retained through 80 meshes was used for proximate analysis.

**2.1 Fibre Morphology:** - For morphological study a small piece of ipomoea Carnea was subjected to chemico mechanical maceration to separate the individual cellular elements from each other without damage. It involves the use of hot acetic acid and sodium chlorite solution to remove most of the lignin and other cementing materials without appreciable degradation of the cellulosic tissue. The microscopic slides of cellular materials were prepared as per BIS: 5285 – 1969. The microscopic slides were projected at a magnification of 40 X and fibre lengths were measured, while the fibre width and cell wall thickness were measured by measuring the projected images at a magnification of 160 X.

**2.2 Extraction of Lignin:** - About 500 gms of screened chips of ipomoea carnea jacq was pulped by soda pulping and soda anthraquinone pulping in a 20 litre stainless steel rotatory digester unit with 25% NaOH (cooking liquor) in 3hrs at a maximum cooking temperature of 170°C at a pressure of 10 psi 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 pH of the obtained black liquor was 12.75 and its density 1.02g/ml. The soda lignin was then precipitated from the concentrated black liquor by acidifying it to pH-2 using various mineral acids at three levels of concentration i.e. 20%, 60% and 100% concentration. The acids used were sulphuric acid, hydrochloric acid, phosphoric acid and nitric acid. The precipitated lignin was then filtered and washed with water and this was adjusted to pH-2 using the acid in earlier step. The soda and soda anthraquinone lignin were precipitated from the black liquor by acidifying it to pH-2. Then the soda lignin was dried in a vacuum oven at 55°C

**2.3 Nitrobenzene Oxidation:** - 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 mixture of soda lignin was transferred to a liquid-liquid extractor for continuous extraction using 10 ml chloroform in order 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 20 ml chloroform. The chloroform was removed by using a rotatory evaporator at 40°C under reduced pressure to obtain nitrobenzene oxidation mixture. The mixture was then dissolved into dichloromethane and made up to 10ml. This mixture was then used as a stock solution for further analysis.

**2.4 Characterization of lignin**:- Characterisation was done by using technique such as infrared (IR), ultraviolet (UV) spectrometry and high performance liquid chromatography (HPLC) to evaluate the cross linked lignin's to cell wall linkages. High performance liquid chromatography (HPLC) was used to analyze the nitrobenzene mixture. Stock solution (0.25ml) was pipetted 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<sub>18</sub> column to identify oxidation product. A mixture of acetonitrile:water (1:8) containing 1% acetic acid was used as an eluent with a flow rate of 2ml min<sup>-1</sup>. The eluent was monitored with an UV (ultraviolet) detector at 280nm. In crystallization process nitrobenzene oxidation the mixture was dissolved into acetone and made up to 10ml. Then the mixture was heated to 60 °C for 10 minutes using hot plate. The precipitate was analysed using IR spectra were recorded with a Perkin Elmer spectrophotometer. 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.

### **3. RESULTS AND DISCUSSIONS:**

With the help of proximate chemical analysis one can have an idea about the test samples of wood that belong to hard wood, soft wood or non woody plants. After the proximate analysis the wood being tested for various parameter such as ash content, alcohol, benzene solubility and many other parameter. Results are shown in Table-1.

Table-2 shows the morphological characteristics of ipomoea carnea. The ipomoea carnea fibres are tapering at one end and slightly less tapering at the other end. The cell wall thickness is very low thus giving a low wall fraction and runkel ratio gives stronger paper. The fiber width and lumen diameter of ipomoea carnea resembles with soft wood like pinus kesiya. The thin walled and wide lumen fibres of Ipomoea carnea collapse easily to double walled ribbon structure on delignification and exhibit plastic deformation, thus offering more surface contact and fiber bonding which gives good physical strength and less porosity.

Soda lignin precipitated by three mineral acids ( hydrochloric acid, nitric acid, and phosphoric acid ) was carried out at concentrations (100%, 60%, 40%). Table-3 shows the yields of soda lignin precipitated by the mineral acids at concentrations 100%, 60%, 40%. The recovery of soda lignin was influenced by the pulping condition, the precipitation and the concentration of mineral acid used for precipitation of lignin. The yield of soda lignin precipitated from hydrochloric acid and nitric acid are in found to be in the range of 1.34-1.37g for each 100 ml black liquor used, this was relatively low as compared to sulphuric acid and phosphoric acid 1.42-1.47g/100 ml black liquor, and observed value indicates that yield is dependent on the number of hydrogen ions in the acid. The presence of hydrogen ions in the acids also affect the yield as phosphoric acid, has three hydrogen ions, gave the highest yield, followed by sulphuric, hydrochloric and nitric acid respectively, hence the acid preferable for precipitating is phosphoric acid.

The standard procedure to analyse lignin is by chemical degradation technique that is nitrobenzene oxidation process. In this process composition of the original polymer can be known. Table-4 shows the analysis in which three monomeric lignin units, such as p-hydroxyphenyl (H), guaiacyl (V) and syringyl (S) which are capable to produce the corresponding degradation product of p-hydroxyl benzaldehyde, vanillin and syringaldehyde were analyzed .The major products found was syringaldehyde and the second major degradation product was found to be vanillin . The total yield of the oxidation products is ranged from 17.5% to 27.4%.

In the Figure1 it is shown that the IR spectra of soda lignin is precipitated by using various mineral acids. The strong and broad band are found at  $3432\text{cm}^{-1}$  which is the characteristic of OH group or phenolic compound. The band seen at  $1334\text{cm}^{-1}$  is due to the bending of vibration in phenolic OH group, but the band at  $1031\text{cm}^{-1}$  is characteristic of a primary alcohol. It is having a clear peak at  $2945\text{cm}^{-1}$  and the band at  $1466\text{cm}^{-1}$  is related to CH stretching of methyl group. Broad medium is shown at  $1711\text{cm}^{-1}$  this is due to the conjugated carbonyl stretching. Two bands at  $1510\text{cm}^{-1}$  and  $1610\text{cm}^{-1}$  are visible ,it is the characteristics of aromatic rings due to skeletal vibrations and the band at  $1110\text{cm}^{-1}$  is mainly due to the ether stretching. A band at  $845\text{cm}^{-1}$  indicates the C-H deformation and ring vibration. A sharp band at  $622\text{cm}^{-1}$  is present only in the spectrum of lignin precipitated from sulphuric acid which is due to C-S stretching, but the spectrum of lignin precipitated from nitric acid shows a sharp band at  $1385\text{cm}^{-1}$  it is the characteristic of N=O stretching. Bands at  $1320\text{cm}^{-1}$ ,  $1230\text{cm}^{-1}$  and  $1110\text{cm}^{-1}$

are corresponding to syringyl units and small bands at  $1270\text{ cm}^{-1}$ ,  $1150\text{ cm}^{-1}$  of guaiacyl units of lignin molecules.

### 3. CONCLUSION:

The study clearly indicates that *Ipomoea carnea* resembles with soft wood. *Ipomoea* can form a potential source of raw material for pulp and paper making. It can be concluded that the thin walled and wide lumen fibres of *Ipomoea carnea* collapse easily to double walled ribbon structure on delignification and exhibit plastic deformation, thus offering more surface contact and fiber bonding which gives good physical strength and less porosity. The presence of hydrogen ions in the acids also affect the yield as phosphoric acid, has three hydrogen ions, gave the highest yield, followed by sulphuric, hydrochloric and nitric acid respectively, hence the preferable acid for precipitating is phosphoric acid. Low concentration of phosphoric acid is preferable as it gives highest yield. From the spectroscopic studies it is observed that phosphoric acid gives the highest absorbance value out of the four acids used in the study.

**TABLE I**  
**PROXIMATE CHEMICAL ANALYSIS OF IPOMOEA CARNE JACQ**

S.No	Particulars	Sample I	Sample II	Sample III	Average	Bamboo
1	Ash content	6.14	6.20	6.10	6.14	4.1
2	Cold water solubility	8.43	6.21	7.53	7.39	6.42
3	Hot water solubility	12.60	12.05	14.10	12.9	5.8
4	Ether solubility	3.04	3.70	3.14	3.29	1.2
5	Alcohol benzene solubility	8.46	7.95	7.45	7.99	4.3
6	1%NaOH solubility	28.6	28.4	29.4	28.0	26
7	Pentosan content	17.60	16.89	16.9	17.12	17.7
8	Lignin content	18.08	18.01	18.00	18.03	26.2
9	Holocellulose content	67.49	66.5	66.9	66.96	67.3
10	Hemi cellulose content	22.40	22.67	22.89	22.65	22.1
11	Alpha cellulose content	46.45	47.45	47.28	47	37
12	Acetyl content	4.32	4.49	4.59	4.46	-
13	Methoxyl content	4.76	5.25	4.79	4.93	-
14	Uronic anhydride	3.45	3.45	3.78	3.56	-

TABLE 2

## MORPHOLOGICAL CHARACTERISTICS OF IPOMOEA CARNEA

S.No.	PARTICULARS	SAMPLE I	SAMPLE II	SAMPLE III	AVERAGE	BAMBOO
1	Basic Density	0.29	0.30	0.30	0.29	0.52
2	Fiber Length	0.68	0.63	0.69	0.66	1.70
3	Fiber Width	33.18	33.0	32.4	32.86	23.60
4	Lumen Width	30.00	28.42	24.5	27.6	9.50
5	Cell wall thickness	1.40	1.50	1.58	1.47	7.00
6	Flexibility coefficient	110.6	116.11	132.24	119.65	248.42
7	Ratio of length to width	0.020	0.019	0.021	0.020	72.03
8	Ratio of twice cell wall thickness to fibre width	0.084	0.09	0.097	0.089	0.59
9	Wall fraction	8.4	9	9.7	8.9	59.30
10	Runkel ratio	0.093	0.105	0.128	0.106	1.47
11	Ratio of wall thickness	0.046	0.052	0.064	0.053	0.74

TABLE 3

## AVERAGE YIELD OF LIGNIN RECOVERED BASED ON gm/ml BLACK LIQUOR

CONCENTRATION	SULPHURIC ACID	HYDROCHLORIC ACID	PHOSPHORIC ACID	NITRIC ACID
100%	1.43	1.38	1.48	1.24
60%	1.44	1.36	1.48	1.23
20%	1.48	1.41	1.54	1.29

TABLE 4

**YIELD AND MOLAR RATIO OF DEGRADATION PRODUCTS OF THE SODA LIGNIN BY  
NITROBENZENE OXIDATION**

PARAMETERS	SULPHURIC ACID			HYDROCHLORIC ACID			PHOSPHORIC ACID			NITRIC ACID		
	20	60	100	20	60	100	20	60	100	20	60	100
Acid Concentration in %												
Oxidation product (% w/w to the internal standard)												
P-hydroxybenzadehyde (H1)	1.3	0.8	0.7	1.0	0.7	0.8	1.2	1.0	0.9	1.0	0.9	0.7
Vanillin (V1)	9.8	8.5	6.1	9.7	7.8	9.2	10.1	9.3	8.1	7.8	5.3	5.6
Syringaldehyde (S1)	10.6	10.2	7.3	11.1	9.6	10.5	11.1	12.0	10.8	9.3	6.8	7.1
p-hydroxybenzoic acid (H2)	0.2	0.3	0.1	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.3	0.2
Vanillic acid (V2)	1.0	1.0	0.5	0.9	0.9	1.1	0.8	0.9	1.2	1.0	1.1	1.1
Syringic acid (S2)	2.2	2.3	2.5	3.0	2.5	2.5	3.9	3.4	3.0	3.8	2.7	3.2
<b>(H1+V1+S1+H2+V2+S2)</b>	25.1	23.1	17.2	26.1	21.9	24.5	27.4	26.9	24.3	23.1	17.1	17.9
Molar ratio: S/H	8.58	11.36	10.6	10.07	11.0	10.83	9.37	14.61	11.5	12.46	7.91	11.44
Molar ratio: V/H	7.2	8.63	7.4	7.28	7.90	8.58	6.81	7.84	7.75	7.33	5.33	7.44
Molar ratio: h/H	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
<b>S=S1+S2; V=V1+V2; H=H1+H2</b>												



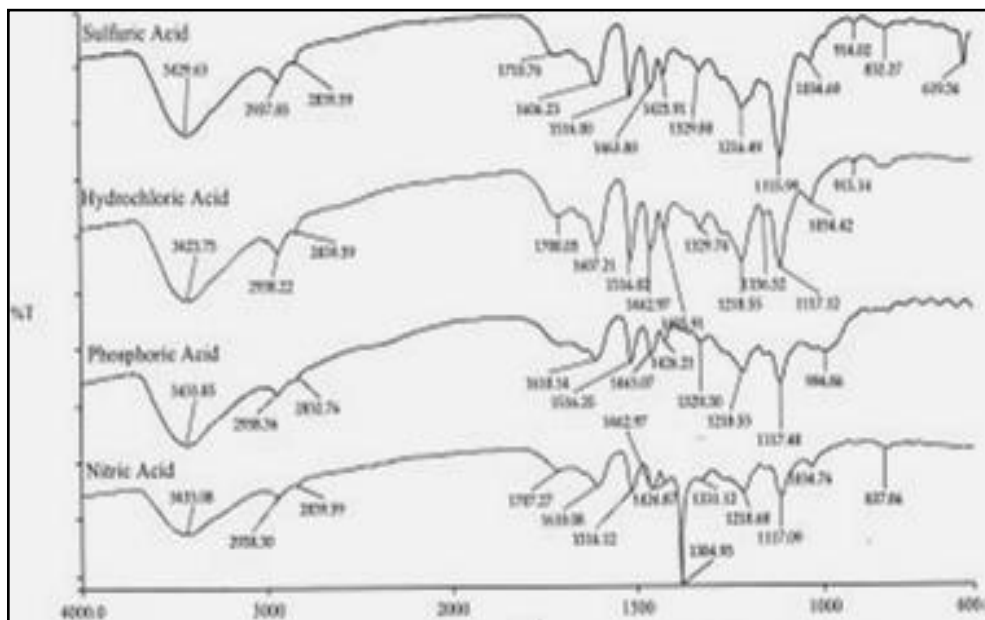
**FIGURE 1****INFRARED SPECTRA OF SODA LIGNIN PRECIPITATED FROM MINERAL ACIDS**

Figure 1: InfraRed spectra of soda lignin of ipomoea carnea precipitated from mineral acids

**REFERENCES:**

1. Preeti Nair, Shukla R.N., Indian J Applied & pure Bio, vol.19 (2):189-195 (2004).
2. Ipomoea Carnea ,The wealth of India, CSIR Publication ,Raw material I,vol.5.,Pg 58,(1950)
3. Sun, R.C., J.Tomkinson and G.L.Jones, Fractional characterization of ash lignin by successive extraction with organic solvents, polymer degradation and stability, 68:111-119, (2000)
4. Venica.A. C.LChen and S.Gratzl Delignification of Hardwood during: Reaction, mechanism and characteristics of dissolved lignin's during soda aqueous pulping of poplar, Tappi Proceedings, pp: 503(1989).
5. Preeti Nandkumar,Studies on the chemical constituents and the pulp and paper making characteristics of Ipomoea carnea jacq ,Oriental Journal of Chemistry,Vol 27,No (1):Pg 149-154,(2011).
6. Shukla R N and Shrivastva R M,Oriental Chemistry 5(3) : 258 (1989).

7. Wan Rosli,W.D and Law,K,N,Cellulose Chemistry and Technology,Vol 32,pp 133-143,(1988).
8. Preeti Nandkumar, Lignin from Soda Liquor and Soda Anthraquinone Liquor of Ipomoea Carnea Jacq, Australian Journal of Basic and Applied Sciences, 3(2): 474-476, 2009
9. Blain, T.J. Anthraquinone Pulping: Fifteen Years Later,” TAPPI, 176(3): 137-146.(1993)
10. Preeti Nandkumar,Comparitive Study between soda lignin and soda anthraquinone lignin in terms of Physicochemical properties of Ipomoea carnea jacq International Journal of chemical environmental and pharmaceutical research,Vol.2,No.1,26-29,January-April,2011
11. Stephen,Y.L and Carlton,W.D,Methods in lignin Chemistry,1<sup>st</sup> edition ,Springer Verlag ,Germany.