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Thermal studies on isolated and purified lignin

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Abstract

The isolation, purification and characterisation of pure lignin, extracted from black liquor obtained from a large pulp and paper mill, are reported. The ultimate analysis of the purified lignin, resulting in 0.3% ash content, confirms its quality as being comparable to any high-grade imported lignin. Thermal analysis resulted in an activation energy of 29.87 kJ mol^{-1} for the thermal decomposition of pure lignin; this is discussed. Detailed IR spectroscopic, XRD and DTA/DTG analyses of the lignin sample are also presented.

Keywords: Lignin; Black liquor; Thermal studies; Activation energy

1. Introduction

Lignin is the second most abundant renewable organic matter on earth, immediately after cellulose, which it accompanies in wood, straw and other plant tissues. The amount of lignin in plants varies widely, and is normally in the range of 20–30% by weight. In chemical structure, lignin is essentially a phenyl-propane-based polyether. In admixture with hemicellulose, it forms the cementing material for cellulose fibrils and imparts strength to the structural elements of the plants. Commonly available lignin products are obtained from the black liquor generated in vast quantities as a by-product of chemical wood pulping [1].

Considerable efforts have been made to utilise the waste lignins as a raw material for many chemical industries. In Europe, out of 50 million tonnes (MT) of technical lignins produced annually, about 3 MT of lignosulphates and 0.1 million tonnes a alkali lignin are used for purposes other than fuel [2]. Pure lignin has recently been used for many

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new products like resins [3, 4], adhesives [5, 6], and polymers [7, 8], etc. However, further advances could be made possible by using lignins in a pure form with known characteristics, because lignin composition varies from biomass to biomass and also depends on the chemical pulping process used for the biomass [9, 10]. Pure lignin is, however, not being commerically produced in India so far.

This paper presents the method of isolation, purification and characterisation of lignin extracted from black liquor obtained from a large-scale paper unit of Ballarpur Industries Limited (BILT) at Choudwar, District Cuttack, in Orissa. BILT uses the sulphate process for pulping soft wood for paper making. The characterisation studies of lignin include ultimate analysis, IR analysis and XRD analysis. Differential thermal studies have also been carried out to evaluate its activation energy.

2. Characteristics of black liquor

Effluents from the pulping process of pulp and paper mills are dark brown or black in colour and hence are called black liquor. The black liquor mainly consists of both organic and inorganic, dissolved and suspended solids along with unreacted chemicals used during the pulping. The suspended matter is mostly cellulose-containing fibrils. The black liquor in the sulphate process is highly alkaline having a pH in the range of 10–12, but the spent sulphite liquor is highly acidic with pH varying from 3 to 4. The total solids in black liquor vary between 50 and 200 g l^{-1}. The water pollution load of pulp and paper mill effluent includes a wide variety of chemicals like lignin, sodium sulphate, sodium bisulphate, chlorine, fillers like talc, kaolinite, titanium oxide, aluminium sulphate and trace metals like Cr, Hg, Pb, etc., depending on the nature of raw materials used and the manufacturing process adopted. The elemental analysis of the black liquor sample obtained from BILT is shown in Table 1.

3. Isolation and purification of lignin

The lignin present in the black liquor is precipitated by lowering the pH to about 3.0 with a suitable mineral acid. The precipitate is thoroughly washed with water to neutralise its acidic character and dried. The dried lignin is treated by successive

Table 1
Elementary analysis of black liquor (BILT)

Elements	Amounts/mg l^{-1}
Lithium	0.01
Sodium	0.66
Potassium	1.17
Magnesium	0.62
Copper	0.38
Mercury	1.89

chemical extraction for removal of impurities, e.g. with ether to remove fats and fatty acids, and subsequently with alcohol–benzene mixture (1:2) to remove the dyes and colouring matter. The extracted lignin is dried and powdered and then treated with 72% sulphuric acid for about 30–45 min, and the contents diluted to 3% strength of the acid. It is filtered and repeatedly washed with hot water. The residue thus obtained is dried to yield pure lignin. Pure lignin serves as a raw material for many useful, newer industrial compounds.

4. Ultimate analysis

The ultimate analysis of lignin to evaluate its ash content was carried out in a precision muffle furnace with slow heating to reach the final temperature of 1000°C. The final temperature of the furnace was maintained for 2 h. The ash content of lignin was found to be 0.3%.

5. IR analysis

The infrared (IR) analysis of lignin carried out using a Perkin-Elmer IR Spectrophotometer is shown in Fig. 1. The IR spectrum is in complete agreement with the standard curve [6]. Although the spectrum contains many absorbtion bands not all can be assigned unequivocally to structural groups. The fingerprint region lies between wave numbers 2000 and 800 cm^{-1}. The presence of methoxyl groups is indicated by the peak in the range 2860–2850 cm^{-1}.

The peak at 1725–1660 cm^{-1} indicates carbonyl (C=O) stretching frequencies and that at 1665 cm^{-1} shows the additional aldehyde or ketone carbonyl group. Among the other specific peaks, one at 1270–1260 cm^{-1} shows aromatic methoxyl C–O stretching and that at 1230–1215 cm^{-1} represents aromatic phenyl C–O stretching. The range of bands for rings conjugated with carbonyl group is found at 1500–1400 cm^{-1}. The 1,3,4-tri-substituted aromatic ring is indicated at 1150 cm^{-1}. Other significant peaks in

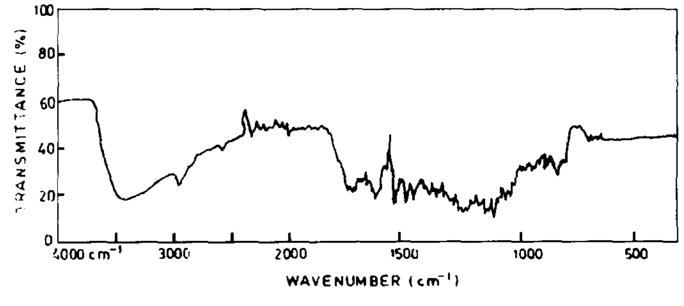

Fig. 1. IR spectrum of lignin.

the lower wave number region include dialkyl ether linkages, –OH group variation and aliphatic ether linkages, and secondary –OH groups.

Comparison of the spectrum with standard curves permits many assignments to be made; however, the structure of lignin cannot be deduced solely from spectral evidences. Indeed, the structure of lignins appears to vary with genera and within single species. Furthermore, native lignin is not identical with whole wood. Although no lignin can be selected to represent protolignin, spectral studies can be of service in assessing changes in structure resulting from chemical reaction.

6. XRD analysis

The purity of the lignin sample greater than 99% has already been established above. X-ray diffraction studies were carried out using a Phillips APD 1710 series X-ray diffractometer. The diffraction pattern shown in Fig. 2. is a very diffused pattern of two or three halos, similar to that of resin compounds. The lignin apparently amorphous, highly cross-linked and has a high molecular mass.

7. Differential thermal analysis

The differential thermal analysis was carried out on a Netzch Model 409 thermal analyser. The experiment was carried out at a sensitivity of 50 mg (TG) and 200 mV (DTA). Samples of 50 mg were heated in a platinum crucible to 973°C at a heating rate of 10°C min^{-1}. Because the thermal analysis was carried out at varying temperature scanning from room temperature to 973 K, the relation between the activation energy

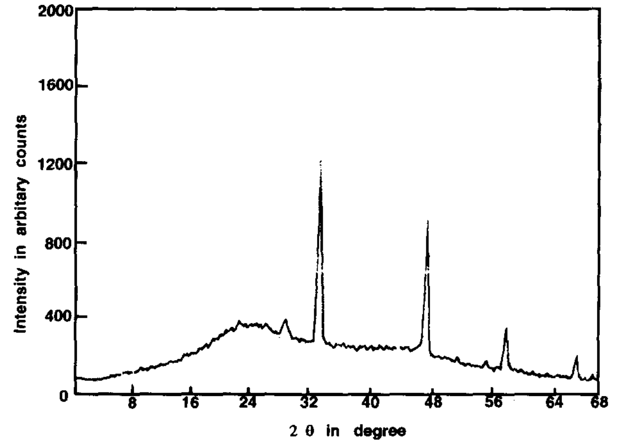

Fig. 2. X-ray diffraction spectrum of lignin.

E_a, the rate constant and the pre-exoponentional factor A is given by the equation

$$d\alpha/dt = A\exp(-E_a/RT)f(\alpha) \qquad (1)$$

where α is the fraction of the total sample reacted at any time t, $f(\alpha)$ is a function dependent on reaction mechanism, and R and T are the gas constant and the temperature of the reaction in Kelvin at time t, respectively.

Assuming the order of the reaction to be first-order, i.e. $n = 1$, and $f(\alpha) = (1-\alpha)$, we can write Eq. (1) as follows

$$\ln[(d\alpha/dT \cdot dT/dt)/(1-\alpha)] = \ln(A) - E_a/RT \qquad (2)$$

The plot of the left-hand side of Eq. (2), $\ln[(d\alpha/dT \cdot dT/dt)/(1-\alpha)]$ is equal to "K" and plotted as a function of the reciprocal of the temperature (T) as shown in Fig. 4 leads to a straight line whose slope yields the value of the activation energy E_a and the intercept gives the value of the pre-exponential factor A.

8. Results and discussions

The most convenient methods for isolating lignin from the black liquor have been used, based on hydrolysis and solubilisation of the polysaccharides with strong mineral acids leaving a residue which, after washing and drying, is termed lignin. Extraneous materials which might go with the lignin must be removed before the acid treatment. However, no unique method of separating lignin from all the other components has yet been found. Lignin isolated by various methods is basically designated by the procedure used for isolation. Moreover, the lignin is altered during isolation by acid hydrolysis and is no longer identical to the protolignin found in the original wood.

The initial lignin precipitated from black liquor as lignin-related compounds (LRC) is not completely free from impurities. The fatty acids and rosins present in LRC are extracted with ether. The subsequent extraction with ethanol–benzene mixture removes the colouring material from the lignin which is mainly due to the presence of dyes and other related compounds. The final product thus obtained is almost a pure lignin. An ash content of 0.3% in the above indicates that the extent of the inorganic elements salt impurities present in the lignin is limited to within 0.3% only.

The IR spectrum of the lignin sample obtained by acidification of the black liquor by hydrochloric acid and shown in Fig. 1 conforms with the standard curve [6]. Spectral absorption bands in the infrared at 1600–1700 cm^{-1} (two bands), 1400–1500 cm^{-1} (a triplet), 1100–1300 cm^{-1}. (five intense bands) and 800–850 cm^{-1} (two bands) are common to both native and condensed lignin, and appear to be sufficiently characteristic that they can be used for identification of lignin.

The X-ray diffraction pattern recorded using a Philips APD 1710 series X-ray diffractometer for the above lignin sample shown in Fig. 2 is a very diffused pattern of two or three halos, similar to that to resin compounds and confirms that lignin is an amorphus polymer. Some studies on lignin have been reported by Harris et al. [11] and demonstrated that the spacing corresponding to the inner halo varies with the material from 6.5 to 12 Å for methylated methanol maple lignin. The substances that separate out from the living cells to become membranes converings, skeleton, etc., form a graded series that extends from some simple inorganic salts to bodies that approximate in complexity that of living matter itself.

Among these substances, lignin possesses two distinguishing characteristics which, to a certain extent, are in common with living matter. It is apparently amorphous, highly crosslinked and has a high molecular weight. A comparison of the sturcture, and of what is known of the crystalline pattern living matter with the structure and the crystalline pattern of the substances secreted by living matter and accumulated in the tissues, is expected to elucidate the dynamics of that fundamental vital process which is so little known, protoplasmic secretion.

Fig. 3 shows the TGA and DTA studies of the sample. The DTA thermogram is characterised by two endothermic troughs and two peaks. The two endothermic peaks are at 100–180°C. The first exothermic peak at 200°C, reaches a maximum value at 500°C and ends at 600°C. The activation energy E_a and the rate constant K of lignin evaluated from Fig. 4 have been found to be 29.87 kJ mol^{-1} and 5.8 respectively. The above activation energy is well within the range of the values reported by Henryk. Struszezyk [9]; and the pre-exponential factor A is 0.6310.

Isolated lignin can serve as the starting material for a series of useful industrial products, namely aromatic compounds and a new class of polymers. The macromolecular, multifunctional nature of lignins makes it very suitable for a wide variety of thermosetting network polymers, slow-release pesticides and many more new

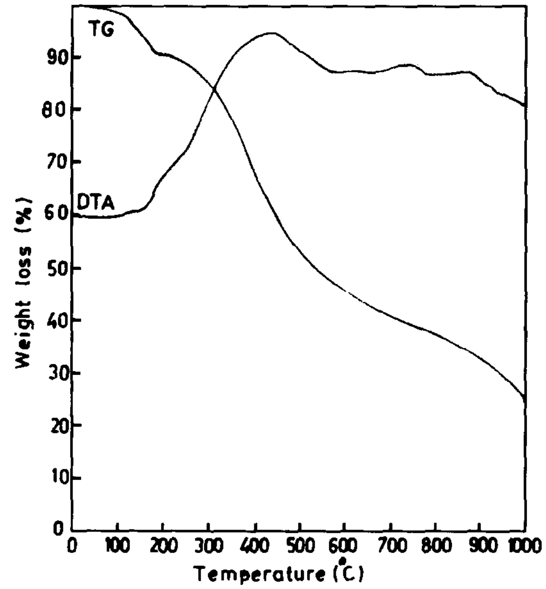

Fig. 3. Thermogravimetric analysis of lignin.

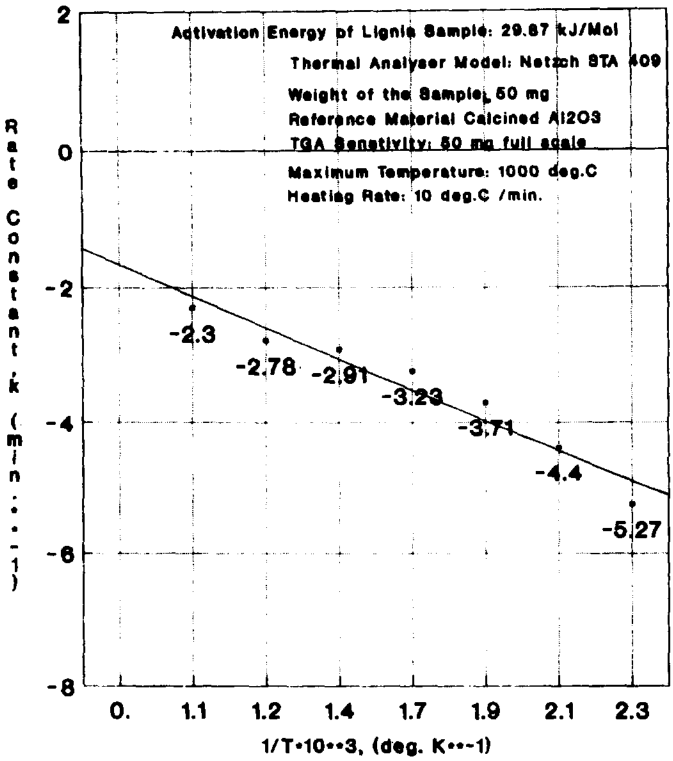

Fig. 4. Modified Arrhenius plot for lignin from dynamic TGA data.

products. The extent to which lignin can become a component of a new polymer may depend upon its reactivity and its solubility with other compounds.

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References

[1] O. Faix, Papier/Dramstadt, 12 (1992) 733–40.

[2] J. Pranda, M.M. Micko, R. Brenzy and M. Kosik., Structure/performance studies on Krabt lignin as a component of Lignin-phenol formaldehyde resins 1st European Workshop, September 1990, Hamburg, Germany, p. 91–96.

[3] Zhao-Xia Guo, A. Allessandro Gandini and F. Pla, Polym. Int., 27 (1992) 17–22.

[4] Zhao-Xia Guo and A. Allessandro Gandini, Euro Polym. J., 27 (1991) 1117–1180.

[5] J.R. Obst and T. Kent Kirk, in A. Willis and S.T. Kellogs (Eds.), Methods In Enzymology-Biomass, Part b, Academic Press, San Diego, CA 1988, p. 3–12.

[6] T. Kent Kirk and J.R. Obst in A. Willis and S.T. Kellogs (Eds.), Methods In Enzymology-Biomass, Part b, Academic Press, San Diego, CA, 1988, p. 87–101.

[7] M.M. Nassar, J. Chem. Tech. Biotechnol., 34A (1984) 21–24.

[8] W.G. Glasser and S. Sarkanen (Eds.), ACS Symposium Series No. 397, Washington DC, 1989.

[9] N. Henryk Struszezyk, Lignin Properties and Materials, American Chemical Society, 1989, Chapter 18, p. 245–261.

[10] N. Sahoo, M.K. Nayak, R.S. Rohella, S.C. Paul and V. Chakravortty, National Seminar on Safe Environment, C.E.T. Bathinda, April 12, 1995.

[11] G.L. Clark, Applied X-rays, 14th edn., (1955) McGraw, New York.