Preparation of Value-Added Products From Black Liquor

Sahoo N.*, Rohella R.S.*, Choudhury S.*, Paul S.C.* and Chakravortty V.**

ABSTRACT:-- Black liquor, a major by-product of pulp and paper industry, has been considered a low economic value product till now and has not been paid much attention for its potential applications. Since it is rich in plant polymers like lignin which is complex in nature and does not easily biodegrade which therefore, creates environmental pollution. The annual national availability of black liquor from the kraft mill alone is about five million tonne which contains more than one million tonne of lignin. Its vast availability and the technology presently available for its chemical conversion and or modification has now completely reversed its economic value.

Chemically, lignin is a three dimensional highly branched aromatic biopolymer of polyphenolic propane, comprising of phenyl propane monomer. Being the main constituent of black liquor, it is a good source of many interesting and valuable aromatic and aliphatic chemicals and newer industrial products.

The present paper describes a method for the isolation and purification of lignin from black liquor. The various characteristics studies like IR, XRD and ultimate analysis of lignin obtained above speaks of its purity and grade since it contains ash not more than 0.3%. A laboratory scale process for the preparation of an universally appreciated aroma chemical "vanillin", from black liquor has been presented. The other R&D activities for the utilisation of black liquor/lignin have been discussed.

INTRODUCTION

In countries with relatively large chemical pulp industries, black liquor, the liquid effluent discharged during pulping process, represents a significant national resource. For a long time black liquor was considered to be of low economic value and hence, little attention was paid to its potential applications as a valuable material. Further, the black liquor being rich in plant polymers like proto-lignin, milled wood lignin and kraft lignin etc. which are complex in nature, do not easily biodegrade and thereby create environmental pollution [1].

The annual national availability of the lignin in black liquor from the kraft mill in India alone is more than one million tonne. Its vast availability and the technology available for its chemical conversion has now reversed its economic value. The R&D work carried out during last one decade in various

* Regional Research Laboratory
BHUBANESWAR-751 013

** Dept. of Chemistry,
Utkal University,
BHUBANESWAR-751 004

fields viz. Petrochemicals, aromatic and polymer chemistry and agriculture, etc. has promoted the usage of black liquor as a raw material for many useful and speciality products in more eco-friendly manner.

Paper industry is one of the most polluting industry and significant proportion of solid and liquid wastes are generated. For every one ton of paper produced by sulphite and/or sulphide (kraft) process, an equal amount of organic solids in kraft black liquor consist of lignin and polysaccharide degraded products (aliphatic carboxylic acids together with a minor fractions of extractives). The non-lignin portion of the black liquor contains mainly sugars and other inorganic undigested salts. The presence of benzene nucleus, the propane side chains of poly propane monomers in the lignin macromolecule, suggest that these are a potential source for making aromatic and aliphatic compounds [2]. Further, the pure lignin also serves as a raw material for manufacture of many industrial compounds which are otherwise not possible to think of.

The work on bio-degradation of lignin in the pulp and paper mill effluents for pollution control and the utilisation of black liquor/lignin for the preparation of various value added products is being carried out in this laboratory for quite some time and significant progress has been made in this direction. The present paper describes a mathod for isolation and purification of lignin from black liquor. Further a lobratory scale process has been developed to prepare vanillin, the most universally appreciated aroma chemical having a variety of industrial and pharmaceutical applications.

CHARACTERISTICS OF BLACK LIQUOR

The liquid waste generated from the pulping section commonly known as black liquor consists of both organic and inorganic dissolved solids and undigested chemicals. The effluent is dark brown or black in colour and hence known as black liquor. In sulphate and soda process,the black liquor is highly alkaline with pH in the range of 10-12, while the spent sulphite black liquor is highly acidic in nature with pH ranging from 3-4. The total solids in black liquor vary between 50 to 200g/l and the suspended matter mostly contains fibres, quartz and sand, etc.. The waste waters from the pulp and paper mill contain a range of chemicals like in lignin, sodium sulphate, sodium bisulphate, chlorine, filler materials like talc, kaolinate, titanium oxide, aluminium sulphate along with trace metals like Cr, Hg, Pb etc. depending upon the nature of raw materials and the manufacturing process adopted. A typical elemental composition and heating value of the black liquor solid obtained from a pulping industries is given below in Table-1

Table-1

Composition and Heating Value of Black Liquor Solids

ELEMENTS	PERCENT
Carbon	42.6
Oxygen	31.7
Hydrogen	3.6
Sodium	18.3
Sulphur	3.6
Heating Value, (kJ/kg of dry solid)	15,400

There are two pulp and paper mills very close to RRL Bhubaneswar, namely Ballarpur Industries limited (BILT) at Choudwar in Cuttack and Konark Paper Industries Limited (KPIL), at Basta in Mayurbhanj district of Orissa. BILT at Choudwar was earlier known as the Titagarh Paper mill and was established in 1960 and its production capacity is 19,200 tonnes of various types of paper per annum. It uses soft wood for the manufacture of quality papers. The mill is presently recovering undigested chemicals and black liquor from effluents of different sections for reuse. It discharges about 15,000 m of waste waters per day. Since BILT has installed an effluent treatment plant, the lignin content in the effluent is quite low.

KPIL established in 1984 is utilising 50 MT of paddy straw or sabai grass and about 20 MT of waste paper per day as raw material. The mill basically utilises the sulphite process and is discharging 2 tonnes of solid waste and 1200 m of liquid waste water per day. Since KPIL has so far not installed any effluent treatment plant and is also not recovering chemicals, the lignin content in their waste water is high. The elemental analysis of black liquor samples obtained from the above two pulp and paper mill units carried out by Atomic Absorption Spectrophotometer are shown in the Table-2.

Table-2

Elemental Analysis of Black Liquor

Elements	BILT Choudwar	KPIL Jharia
Sodium, mg/l	0.66	0.30
Potassium, mg/l	1.17	0.94
Magnesium, mg/l	0.62	0.46
Lithium, mg/l	0.01	0.01
Copper, mg/l	0.38	0.38
Mercury, µg/l	1.89	1.89

PRESENT STATUS OF LIGNIN UTILISATION

Despite many years of investigations regarding the properties and uses of lignin in black liquor, only a small fraction of it is currently utilised. Until the 1980's, a large amount of lignin was being discharged into streams and waterways as dilute aqueous solutions. However, such a disposal is no longer permitted and almost all the effluents containing lignin are concentrated and presently burnt as fuel. Many investigations have been aimed at production of newer chemicals from the lignin waste. Until recently, most of the above processes were uneconomical when compared to processes which utilise petroleum and other fossil fuels. Owing to rapid depletion of fossil fuels resulting in cost escalations, renewed interest is being shown in the use of lignin as a raw material for the production of chemicals, especially aromatic compounds and industrial products.

Till now the organic matter of kraft black liquor has only one form of utilisation. After separation of extractives, the concentrated liquor is combusted in the recovery boiler, since energy is obtained from the organic matter, while the inorganic components are simultaneously converted into compounds for re-use, or for regeneration into the cooking chemicals. However, in this way the black liquor utilisation as fuel is not economical. Also the capital costs of the kraft recovery plant is also very high.

Lignin in spent liquor is usually called waste lignin. Such a designation may have been valid during the period when the fuel cost was low. With the rapid increase in energy cost associated with increase in petroleum products lignin in black liquor has a greater importance as fuel. Therefore, lignin should not be termed a waste and processes aimed at extraction of the lignin for various applications must be taken into consideration [3].

EXPERIMENTAL METHODS

1. Extraction and Purification of Lignin

The solid precipitation of the black liquor, otherwise called Lignin Related Compounds (LRC) is precipitated by lowering the pH value of the liquor by a suitable mineral acid. This precipited residue is then thoroughly washed with water to neutralise its acidic effect and then dried at room temperature. The dried substance is treated for successive chemical extraction. First of all the ether extraction is done to extract the fat and fatty acids followed by alcohol-benzene extraction to extract the dyes and colouring materials of lower value added products from the compound. Finally the residue is dried and powdered resulting in purified lignin. This purified lignin is then characterised by different spectroscopic and analytical techniques. The method to recover the dissolved inorganic chemicals from the non-lignin filtrate is described below.

The non-lignin filtrates obtained above is evaporated and washed with 10% sodium hypochloride to yield a mixture of inorganic salts like sodium sulphate, sodium carbonate, etc.. The purification of these inorganic salts is also possible with respect to corresponding preliminary radical tests. While the final filtrate of the process being rich in sugars of higher carbohydrate groups and has a high chemical oxygen demand (COD) is being tried for biogas generation.

2. Preparation of Vanillin

Oxidative cleavage of black liquor with a suitable catalyst, modifies the lignin structure to some low molecular products [4-5]. In this method, black liquor was taken with a small amount analar grade cupric oxide (2% wt/wt) in a pressure vessel. The initial pH of the black liquor being 9.5 was raised to 13 by 2M sodium hydroxide. The vessel was then closed and uniformly heated for about two hour. After the digestion, the digested sample was transfered to a separating funnel and washed successively with chloroform and the chloroform extract separately collected. The remaining aqueous layer was acidified with sulphuric acid to bring down the pH to 3 The precipitated unreacted lignin was filtered. The filtrate was successively extracted with chloroform which contain vanillin. The chloroform was distilled to get the vanillin. The confirmatory test for vanillin were carried out with (i) dinitrophenyl hydrazine (DNP) to yield a red colour precipitate and with (ii) ferric chloride solution which gives a blue colour solution with vanillin.

An alternate method for the preparation of vanillin from black liquor is also presented here. The digested black liquor obtained earlier is dissolved in chloroform and exhaustively extracted with saturated sodium bisulphite solution. The vanillin goes into the bisulphite solution with the formation of an aldehyde-bisulphite complex, which on acidification removes sulphur dioxide when air or nitrogen is blown into the solution. The vanillin is then extracted with chloroform as described above.

3. Testing and Analysis of Lignin and Vanillin

Different instrumental analysis were carried out for lignin sample separated in the laboratory to assess its purity, physical characteristics and functional groups. The IR spectra of purified lignin was carried out by Perkin Elmer IR Spectrophotometer and is shown in Fig. 1. The X-Ray Difraction study of lignin was carried out by Philips Holland Make APD 1710 series X-Ray diffractometer and the spectra are shown as Fig. 2. The ultimate analysis was carried out at 1000°C in a precision temperature controlled muffle furnace. The final temperature of the furnace was maintained for 2 hours. The ash content of lignin was found to be 0.3%. Similary the vanillin sample was also tested by chemical methods and instrumental method. The ultraviolet absorption spectra carried out by Jasco Model UV/VIS spectrophotometer 7800 using 1-cm cells in the regions 250 to 500 nm with methanol solution is shown in Fig. 3.

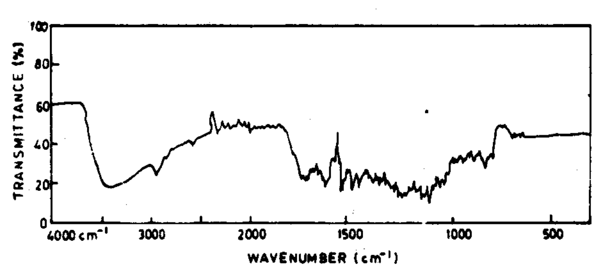

Fig. 1 IR SPECTRUM OF LIGNIN

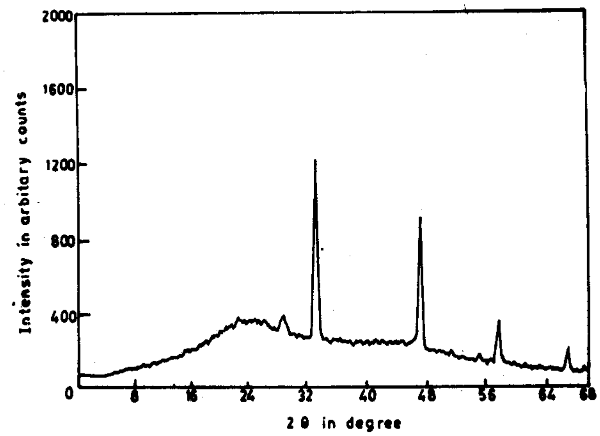

Fig. 2 X-RAY DIFFRACTION SPECTRUM OF LIGNIN

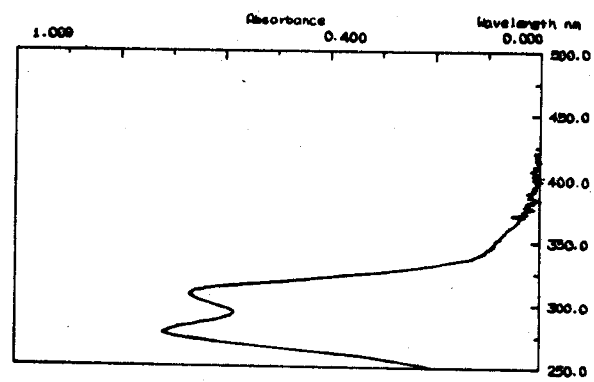

Fig. 3 UV SPECTRUM OF VANILLIN

RESULTS AND DISCUSSION

The removal of the polysaccharides from the digested black liquor by hydrolysis with strong mineral acids leaves a residues containing lignin. However, the lignin in the black liquor is not completely free from the other reactants. The initially precipitated LRC when extracted with solvent ether, removes most of the fatty acids and rosin acids. The subsequent extraction with ethanol-benzene mixture removes the colouring materials which are mainly due to the presence of dyes and other related compounds. The final product obtained is almost a pure lignin. The colour of the isolated lignin varies from a light tan brown to dark brown depending on the method of isolation. The dark colour in alkaline black liquors is mainly due to lignin condensation products.

The IR spectrum of lignin sample obtained by acidification of the black liquor by hydrochloric acid as shown in Fig. 1 which confirms to the standard spectrum [7]. The X-Ray diffraction studies carried out using above lignin sample shown in Fig 2, indicates that lignin is an amorphous polymer, even through it exists in an orderly morphological arrangement in certain parts of the fibres. The ultimate analysis of lignin carried out to evaluate its ash content was found to be 0.3%. All the chemical tests conducted for vanillin sample responds to its presence and the ultraviolet absorption spectra carried out at 250 to 500 nm with methanol solution as shown in Fig. 3 signifies the aromatic aldehyde substitutions by its highest absorbance at 280 nm.

The oxidative cleavage of lignin molecule with cupric oxide in alkaline medium, can be seen to the part with the functional bond of the lignin structure which can be seen to involve loss of one, two or three carbon atoms of guaiacyl propane units. In no case a guaiacyl propane compound seems to have been isolated from the reaction mixtures. It appears therefore that the cleavage of lignin polymer to monomer may always involve cleavage of the β-C and γ-C bond. Yield of guaiacol is generally low indicating considerable stability of the bond connecting to the guiacyl nucleus. The process flow sheet indentified for preparation of vanillin from the black liquor is shown in Fig. 4. The alkaline oxidative cleavage reaction of black liquor/lignin to vanillin is an important use of black liquor as a value added product [8].

LIGNIN AS VERSATILE CHEMICAL FEEDSTOCK

As the lignin molecule contains a number of functional groups and reactive sites, reactive types include primary and benzyl alcohol, phenols, aldehydes, ketones, oleins and ethers, it can be used as a versatile chemical feedstock for many value added products. Reactive aromatic sites include carbons ortho-and para-to phenoxy and methoxy substituents. Therefore, a number of myriad and interesting reactions, such as addition, derivatisation, oxidation reduction, condensation and depolymerisation can be studied for predicting newer and many interesting essential products [9]. It seems to be an attractive material for modification and use for purposes other than the fuel which increases environmental sustainability.. It can provide a number of cheaper aromatic chemicals comparable to synthetics based on petro-chemicals, paints, food additives and agriculture.

Lignin molecule on degradation by solvolysis in alkaline medium offers technically viable ways for the production of low molecular mass industrial solvents like dimethyl sulphide (DMS), dimethyl sulfoxide (DMSO); alkali fusion products includes phenol, carboxylic acids, etc. Fig. 5 shows some of the routes of degradation of this macromolecule.

Further reasearch effort are continuing utilising lignin for thermosetting resins and graft-polymers. The interest is also of incorporating lignins into other thermosetting resins, including polyurethanes.

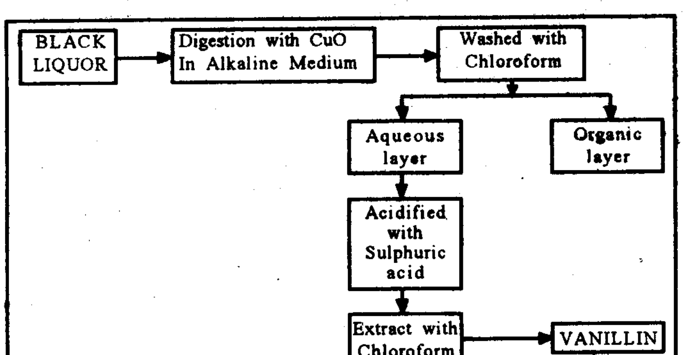

Fig. 4: Process Flow Sheet for Preparation of Vanillin from Black Liquor

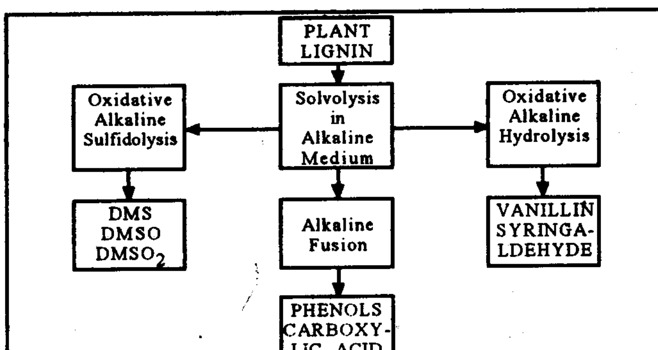

Fig. 5: Degradation of Lignin into Low Molecular Weight Compunds by Solvolysis

polysters, polyamines and epoxies [10]. The work on development of lignin grafted co-polymer with a few selected monomer has been initiated in the laboratory.

CONCLUSIONS

Isolating lignin as a main product from black liquor and using it for other by-products as a new source of many aromatic and aliphatic compounds in relation to future environmental sustainability is the predominent field of research and development of the present time. The present economic and strategic analysis of lignin have lead to many important research and development for use of black liquor in various field of applications. Preparation of vanillin and similar low molecular mass products from the black liquor and isolation and purification of its main polymeric constituent lignin can economically help the pulping process more favourably and eco-friendly manner.

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