Utilization Of Lignin As A Source Of Industrial By-Product To Improve Economics Of Agro Based Mills

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ABSTRACT

Lignin is one of the most abundant renewable resources available as a by-product of pulping process. Most of the lignin obtained from kraft pulping of woody raw material is burned in recovery boilers to fulfill a part or most of energy requirement of the mill. However In the absence of a viable chemical recovery in agro-based pulp and paper mills , un-till last decades, black liquor rich laden effluent was drained as waste ,there by causing severe problems of pollution in these pulp and paper mills.

With imposition of CREP and as per notification / guidelines issued by MOEF, Central Pollution Control Board has permitted the adoption of lignin removal process (LRP) as one of the option to achieve zero discharge and meeting desired Pollution Control Norms. With the adoption of LRP in these small Agro based Pulp& Paper mills (bellow 50 tpd) large quantities of lignin was available as waste biomass. As a result large continent of lignin is available as waste bio mass which if utilized effectively could become a valuable source for various industrial applications. The present article covers the efforts of CPPRI in this direction.

Introduction

The Pulp and Paper Industry is one of India's core sector industries. There are around seven hundred Pulp and Paper Mills producing about 7.0 million tons of Paper and Board of which nearly 33% is contributed by Agro based sector. Performance of the industry has been constrained due to the high cost of production caused by inadequate availability and high cost of raw materials.

In absence of a viable chemical recovery system in small Agro based mills with pulping capacity of less than 50 tpd, discharge of black liquor laden effluent, rich in lignin, was one of the problems faced by these mills, in meeting the discharge norms. Due to its highly complex polymeric structure, the major portion of lignin which is high molar mass and constitutes to more than 75% of the total lignin remains practically a bio-refractory material in all biological treatment processes.

Due to the condensed nature of lignin molecules, it exerts an appreciably high COD (~50%) and color (~90%) values in the spent liquor.

Looking into the stringent discharge standards laid down by Environment Authorities, it is essential that lignin should either be degraded to low molar mass or partially/ completely removed from the effluent streams before being treated in biological treatment systems in order to achieve stipulated standards in terms of COD and color nearer to what is permitted by the concerned Central/ State Pollution Control authorities.

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TABLE-1
TYPICAL CHARACTERISTICS OF AGRO BASED BLACK LIQUORS IN INDIAN PAPER INDUSTRY

Particulars	Mill-1	Mill-II	Mill-III
Size of the mill	50	50	45
Chemical Pulp Production MT/D	45	45	20
Raw material employed	Bagasse, wheat straw & back reed.	Wheat straw	Rich straw
Cooking charge as NaOH,% w/w	13.5	14	5.5
Total Black Liquor solids, MT/D	53.0	54.0	20.0
BLACK LIQUOR CHARACTERISTICS:			
pH at 25oC	9.7	10.2	8.8
TDS.g/l	44.0	42	38
S.S.,g/l	2.0	2.1	4.0
Silica,%w/w as NaoH	25.6	26.0	23.3
Total Organics,% w/w	74.4	74.0	76.7
Lignin,g/l	16.0	13.2	14.4
High/Low molar mass ratio of lignin by Gel chromatography	1.45	1.4	1.2
POLLUTIONAL PARAMETERS:			
COD,g/l	48.7	45.6	40.0
BOD,g.l	15.5	13.8	16.5
COD/BOD	3.36	3.3	2.42
Biodegradability,%	48	55	38

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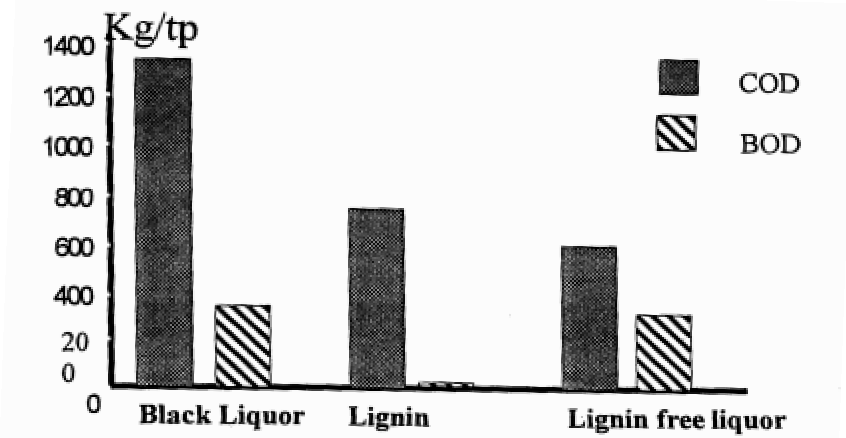
Fig. : 1 GENERALIZED REPRESENTATION OF POLLUTION LOADS OF BLACK LIQUOR AND ORGANICS



meeting desired Pollution Control Norms. Lignin a polymeric aromatic compound has been of major concern to environmentalist during treatment of black liquor laden effluents in biological treatment processes. Whole it constitutes to nearly 50% of the total organic biomass in the spent pulping liquor.

With the advent of lignin removal process and its adoption in various Agro based mills, significant quantities of lignin, a polyphenolic polymeric organic compound, is available as waste biomass which, if utilized, as source of by-product for industrial application, may help the Agro Based Pulp and Paper Mills to improve their economics by way of sale of this valuable by product. As per estimates nearly 15 tons/ day of precipitated lignin is being discharged equivalent to nearly 25 tons of coal per day from a 50 tpd mill. At national level this resource drainage from Agro based mills comes to around 0.6 million tons of coal equivalent per annum.

CPPRI, while working in the area of lignin utilization for last more than a decade, explored various possibilities of utilization of lignin for various industrial applications viz. Phenol-Lignin-Formaldehyde Resin, a source of clean fuel and as retardant in concrete mixture.

The present paper highlights the possibility of utilization of lignin/lignosulphonates for above mentioned industrial application, which should help in improving the competitiveness of agro based mills while improving the environmental status.

Results and discussion:-

Black Liquor: Its Chemical Composition & Magnitude of Pollution

Black liquor is a complex mixture of organic and inorganic compounds with organic to inorganic ratio of 70 :30 .**Table-1** shows the typical analysis of various agro based black liquors. The pollution loads of black liquor, lignin and lignin free spent liquor is shown in Fig-1

Pollution load of black liquor, lignin and other carbohydrates degraded organics:

Further the pollution loads of black liquor and other organic components containing mainly carbohydrates and lignin is shown in **Table-2.** The abnormally high COD/BOD ratio is a clear indication of the fact that lignin is a highly biorefractory material. As during pulping only part of the lignin gets dissolved and the major portion is solubilised as large colloidal macro-molecule. Thus, in biological treatment processes due to the complicated structures of the lignin macro-molecules, the micro-organisms not only remain ineffective in its capacity to biodegrade the lignin structure, but after forming a protective covering on the lignin macro molecules get dormant, thus inhibiting and deactivating the biological treatment efficiency only up to 50% in terms of COD.

Lignin: A biorefractory material in black liquor

During the final pulping stages, significant amount of lignin condensation reactions take place resulting in a high molar mass lignin entity. For instance, comparing the different molar mass components of lignins,viz. in situ, the middle of pulping stages and at the end of cooking, it can be seen that the molar mass of lignin increases appreciably, which results in a complex polymeric structure of lignin in comparison to cellulose, hemicelluloses and organic acids present in black liquor. The different molar masses at each

TABLE-2

POLLUTION LOADS OF BLACK LIQUOR AND ORGANICS

Pollution loads of various components	Bagasse	Rice Straw
Black Liquor:-		
COD,kg/tp	1100	1238
BOD.kg/tp	244	288
COD/BOD	4.5	4.3
Color.kg/tp in PCU	1380	1420
Carbohydrate Rich spent Liquor:		
COD,kg/tp	400	600
BOD.kg/tp	218	269
COD/BOD	1.83	2.23
Color.kg/tp in PCU	82	132
Lignin rich slurry:		
COD,kg/tp	692	619
BOD.kg/tp	16.0	10
COD/BOD	43.25	62
Color.kg/tp in PCU	1291	1282

Table 3

MOLAR MASS DISTRIBUTION OF DIFFERENT STAGES OF LIGNIN

Particulars	Delton
Lignin:	
in situ	1800-2000
Middle of pulping	2000-30,000
Black liquor	>30,000
Hemi celluloses	DP-70-100
Degraded acid of lignin & Carbohydrates	Low molar mass

stage of lignin starting from raw material to the black liquor and other organic molecules in a given in Table:3

Need for Lignin Separation from Black Liquor:-

The effluents containing black liquor discharged in an agro based pulp & Paper mill contain complex mixture of aromatic Phenolic compounds ranging from low molecular weight monomeric to high molecular weight polymeric substances, i.e. lignin and its derivatives. These lignin based compounds contribute to higher pollution loads in terms of COD and color. Based on the studies carried out at CPPRI, it has been observed that molecular size/ weight of the lignin has great influence on the COD values. Due to complex nature, the major portion of lignin which has high molecular weight and contributes to more than 70% of the total lignin remains practically a recalcitrant material and sometimes bioinhibitory too and passes on to the recipient stream, even after biological treatment.

Keeping this in view, need for removal of lignin has been strongly felt to remove only the high molar mass fraction of lignin which is responsible for non biodegradable COD without adversely affecting the biodegradability of the resultant effluent.

Table-4 shows the efficacy of pollution reduction of black liquor in conventional biological treatment systems.

Table-4

EFFICACY OF POLLUTION REDUCTION OF BLACK LIQUOR IN CONVENTIONAL BIOLOGICAL TREATMENT SYSTEM.

Parameters	Pollution Load before biological treatment	Pollution load after biological treatment
Effluent Volume M^3/tp	40#	-
COD, kg/tp	1350	810
BOD, kg.tp	420	126

Utilization of Lignin for Various Industries Application

Studies on Development of Phenol Lignin Formaldehyde Resin

Various percentages of lignin was replaced to Phenol keeping the phenol to Formalin weight ratio constant to 1:18. 10%, 20% and 30% replacement by lignin were adopted in making Phenol Lignin Formaldehyde resin.

The resin was discharged and then the flow properties of PLF resin determined. Properties of resin with different Batches are mentioned in the same table.

Table-5

RESIN FORMULATION AND PROPERTIES OF RESIN

SI.NO.	PARTICULARS	BATCH1	BATCH2	BATCH3
1.	Phenol (98-99%)	180 gms	160 gms	140 gms
2.	Lignin	20 gms	40 gms	60 gms
3.	Flow time in B4 flow cup at room temperature	21.50 seconds	22.9 seconds	27.2 seconds
4.	Water Tolerance	1:14	1:14	1:14
5.	P^H	9.79	10.00	9.91
6.	Solid content	50.47%	50.55%	50.55%
7.	Spread in gms/sqm.	320-350 gms/m^2	320-350 gms/m^2	320-350 gms/m^2
8.	Open Assembly time	65 minutes to bring down glue coated moisture content to 14%-16%	60-95 minutes to bring down glue coated moisture content to 14%-16	60-95 minutes to bring down glue coated moisture content to 14%-16%

Adhesive formulations

PLF resin : 100 parts
CSF : 10Parts
Species : Vellapine veneers of thickness 1.6 mm (1'x1')
Construction : 3 ply
Moisture content of veneer :
Before coating : 6 % - 8%
OAT : As mentioned in **Table-5**
Hot Press temp : 145± 5°Cu
Sp. Pressure : 14 kg/cm^2
Pressing time : 8 minutes

Panels of 4mm thick 1sq ft were made and the panels were subjected to Test as per IS: 848:2006-"Specification for synthetic resin adhesives for plywood (Phenolic and Amino plastics). The properties of are given in **Table-6.**

Lignin- As a source of Clean Energy:

With the rise in the global concerns over economy and environment the use of biomass as a source of renewable energy has assumed greater

Table-6.

Batch No.	Test	Criteria for conformity	Actual observed Results
1.	**BWP GRADE (Boiling Water Proof)** Six cycles: Each cycle consisting of 8 hours boiling in water and thereafter drying at 65±2°C for 16 hours	No separation of plies at the edges and / or surface at the end of six cycles. On forcible separation of plies with knife, wood failure shall be predominate and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed.	No separation of plies at the edges and / or surface at the end of six cycles. 80% wood failure Excellent bond
2.	**BWP GRADE(Boiling Water Proof)** Six cycles: Each cycle consisting of 8 hours boiling in water and thereafter drying at 65±2°C for 16 hours	No separation of plies at the edges and / or surface at the end of six cycles. On forcible separation of plies with knife, wood failure shall be predominant and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed.	No separation of plies at the edges and / or surface at the end or six cycles. 80% wood failure Excellent bond
3.	**BWP GRADE(Boiling Water Proof)** Six cycles: Each cycle consisting of 8 hours boiling in water and thereafter drying at 65±2°C for 16 hours	No separation of plies at the edges and / or surface at the end of six cycles. On forcible separation of plies with knife, wood failure shall be predominant and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed.	No separation of plies at the edges and / or surface at the end or six cycles. 65% wood failure Pass standard

significance. Fuels derived from biomass are considered eco-friendly as they substitute the use of fossil fuels and also offset the fossil fuel related emissions.

High heating value of lignin makes it extremely suitable for use as a bio-fuel. Subjecting the lignin to high temperature produce gases like CO, CO_2, H_2 & CH_4 in varying composition. The principal components of these gases are CO+H_2, commonly known as synthesis gas. The thermo-chemical reactions can be tailored to maximize the yields of synthesis gas. This can be further converted into alternate fuels like ethanol through already established and commercially available technique.

Pyrolysis constitutes one of thermo-chemical process for producing synthesis gas. In pyrolysis, biomass is heated to temperatures ranging from 400-800^{0}c in an oxygen starved reactor. Studies were carried out at CPPRI to explore the pyrolysis route of synthesis-gas production.

Pyrolysis of Lignin

The facilities at one of the identified laboratories for conducting studies on thermal cracking of lignin were utilized to carryout pyrolysis study on lignin. Pyrolysis was carried out on the isolated lignin sample at a temperature of 700^{0}C and the yields of gas, char and tar were determined. The composition of the gaseous products was also determined and characterization of the char produced was carried out. Table-7 gives the composition of the pyrolysis product obtained for the isolated lignin. Table-8 gives the gross calorific value & elemental composition of char produced.

The Study indicated that on pyrolysis, lignin yields a mixture of char , tar and gaseous products. The gaseous products contain substantial amounts of useful hydrocarbon and combustible gases like CO & H_2. The latter is commonly known as synthesis gas that can be used as a precursor for production of clean fuels as ethanol. The char obtained from the lignin pyrolysis was also characterized for its elemental composition which showed enrichment of carbon content, indicating its utility as a solid fuel Table 8.

Lignin/Lignosulphonate as a source of concrete admixture

Efforts are being made at CPPRI to utilize lignin obtained as by-product from spent pulping liquor in agro based mills employing sodium lignosulphonate. Sodium lignosulphonate.from alkaline sulphate pulping could be used as a source of retardant in concrete admixtures. The preliminary studies on evaluation of lignosulphonate indicated good possibility of utilizing these sodium based lignosulphonate as retardant in concrete admixture. Based on the encouraging results obtained, further studies are in progress to evaluate and explore possibilities of its utilization as an additive in concrete admixture .

Table-7:

COMPOSITION OF LIGNIN PYROLYSIS PRODUCTS AT TEMPERATURE OF 700^{0}C

Parameters	Values
Char	52 %
Tar	3 %
Gas	45 %
Gaseous products	H_2 - 6.4 % CO_2 - 11.3 % O_2 - 1.1 % N_2 - 29.1 % CO - 19.9 % HC - 32.4 %

Table-8:

CHARACTERIZATION OF CHAR

Parameters	Values
Gross Calorific Value	3655 cal/gm
Elemental Analysis	Carbon- 42.67 % Hydrogen- 0.72 % Nitrogen- 0.36 % Sulfur- 10.95 %

Conclusion:

The studies carried out at CPPRI show that lignin, a low value product, can be converted into energy , fuels, chemicals or other value added products that give attractive pay-back of lignin removal process and enhance the cost-competitiveness of agro-based mills. Efforts are being made to find economically viable conversion process and technologies for value added lignin by-products .

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