New approach to recovery of chemicals from bagasse pulping liquors.

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ABSTRACT

Most of the agro residue fibrous raw materials like begasse, straws etc. contain invariably higher proportions of hemicellulose contents as compared to woods. During pulping major proportions of these hemicellulose get dissolved and influence the physico-chemical properties of spent pulping liquors. In the present paper an attempt has been made to isolate hemicellulose & silica from spent pulping liquor and improve the qua ity of the resulti g spent pulping liquors. Nearly 12% hemicellulose & 1.7% of silica were isolated by addition of methanol. The studies on resulting black liquor clearly showed that there was a significant improvement in thermal and rheological properties of the black liquor. The paper highlights the findings on the influence of hemicellu ose and also possibly a new approach to recovery of chemicals other than caustic soda.

INTRODUCTION

The operation of the chemical recovery in a pulp & paper industry has a vital bearing on the economics of the mill. Number of small pulp mills based on agro-residue are operating and none of these are equipped with suitable system for chemical recovery. Absence of a viable chemical recovery system is the single most factor for low profitability, heavy recurring losses and severe pollution problem. Net recurring losses, occuring in a small pulp mill of 30 tpd capacity without a chemical recovery system in terms of cooking chemicals & biomas comes out to be as high as Rs. 22 5 million & 7 million/year[1]. The other major loss is that of energy as every ton of caustic need 2000 kwh of electrical energy which results in a loss of about 12000 MW per annum on national level.

With the imposition of stringent legislation by pollution authorities and subsequent impo ition of MINAS tolerance limits, these mills are left with no other alternative except to go for a suitable chemical recovery/treatment system. Weak black liquor (WBL) from small pulp mill is presently disposed as an effluent combined with waste water from other sections in the paper mill. WBL represent 15-25% of the total flow and nearly 70-80% of the total pollution load. It has been estimated that pollution load of a 30 tpd agro-based paper mill making printing writing grades of papers is two-three times more than organic load released by a mill of 100 tpd capacity equipped with a chemical recovery[2].

Application of conventional recovery system involving evaporation & incineration suffers severe set back due to the fact that spent pulping liquors from agro-residues differs substantially compared to those from wood pulping in terms of volume and total solids of WBL, viscosity, colloidal stability of concentrated black liquors and poor rate of thermal decomposition.

During the last two decades, intensive R&D activities have been initiated for the development of simplified chemical recovery systems for small pulp mills.

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However only few of them like copeland fluidised bed combustion has been commercialized. However, these processes did not gain much of popularity for small units, because of certain constraints like high capital input and complexity of operation. The recently emerged DARS process, which is relatively simple and less capital intensive as compared to conventional recovery systems shows promise of potential applications for soda based small mills. This process which involves combustion of mixture of 45% solids black liquor and haematite (Fe_2O_3) ore followed by regeneration of NaOH by water leaching has been tried on laboratory scale at CPPRI but the economic viability of the process is yet to be ascertained on pilot plant and subsequent scaling to small pulp mills.

The main criteria determing the viability of choosen chemical recovery system are :

— Productive capacity of the mill should meet minimum economic limit.

— technical feasibility of process choosen and

— magnitude of pollution.

In recent years, most of the chemical recovery units are over loaded and efforts for partial reduction of load, by way of separation of some of the organic components which will not effect the thermal efficiency are going on.

In the present paper an attempt has been made in similar direction. The raw material choosen is bagasse as it is going to be the mainstay of agro-based pulp & paper mills.

EXPERIMENTAL

Spent liquor preparation : Spent liquor was obtained from soda pulping of depithed bagasse at 160°C for 1 hr, with 16% sodium hydroxide.

Isolation of hemicellulose : Hemicellulose was isolated according to method followed by Venter[3]. The spent liquor was mixed with an equal quantity of methanol on weight basis. After heating to 60°C and cooling, the hemicellulose precipitate was centrifuged, washed twice with 50% aquous methanol and air dried. Original black liquor, liquor obtained after hemicellulose precipitation, and hemicellulose were analysed for various thermal & physico-chemical properties.

Chemical analysis : Chemical analysis of spent liquors & precipitated hemicellulose was carried out according to the procedures mentioned in TAPPI Standard Method T-625.

Gel Chromatography : Gel filtration experiments were carried out using LKB Pharmacia gel chromatograghy unit provided with automatic UV-detector, the chart recorder and the fraction collector, Black liquor sample free from suspended matter and equivalent to 35 mgs of total solids were charged to 1.6 Cm × 60Cm column of sephadex G-25. This charge was eluted through column by bicarbonate-hydroxide buffer at a flow rate mainianed at 29 ml. per hour using peristaltic pump.

PHYSICO-CHEMICAL PROPERTIES

Viscosity measurement : Dynamic viscosity of the spent pulping liquors was measured on Haake rotational Model viscometer RV-20. The measuring system used was M5 having a maximum torque of 4.9 N.Cm and the sensor system employed was NV. Precision thermostatic circulator was used to maintain constant temperature ($\pm$0.1°C) during viscosity measurements.

THERMAL PROPERTIES :

Swelling volume ratio (SVR) : SVR Value of spent liquor was measured according to the method followed by oye; etal[4].

Calorific Value : Calorific value of spent liquor was determined according to TAPPI-Standard method T-605 used for the analysis of coal.

Ignition Temperature (Tig) : Temperature of ignition at which the char burning commences was measured using STA-781 thermal analyser. The temperature at which DTA peak appeared is taken as "Tig"[5].

Integral Procedural Decomposition Temperature (IPDT) : IPDT is the temperature at which the half of the total polymer is decomposed. The IPDT is measured according to the procedure described by Wandalt[5].

RESULTS & DISCUSSION

Raw material chemical composition : Spent liquor properties from agricultural residue like bagasse, cereal straw, differ substantially as compared to wood black

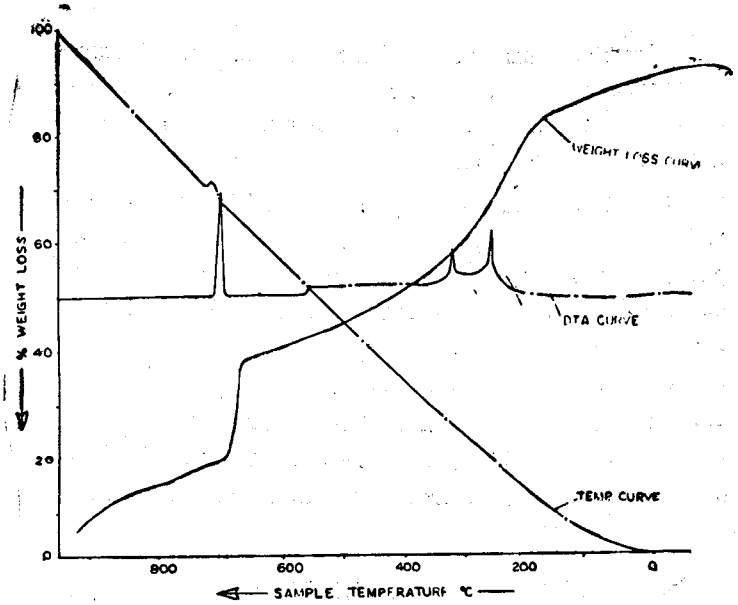

FIG. 1, TG & DTA Curve of Black liquor Hemicellulose.

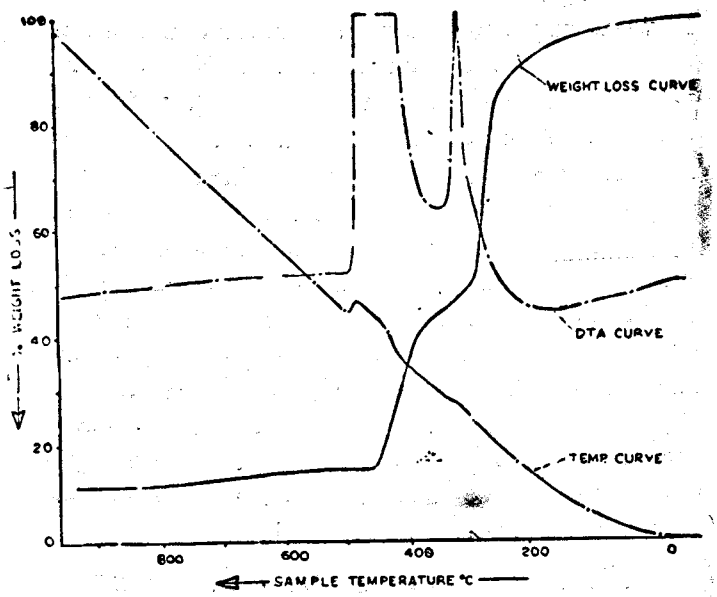

FIG. 3, TG & DTA Curve of Hemicellulose

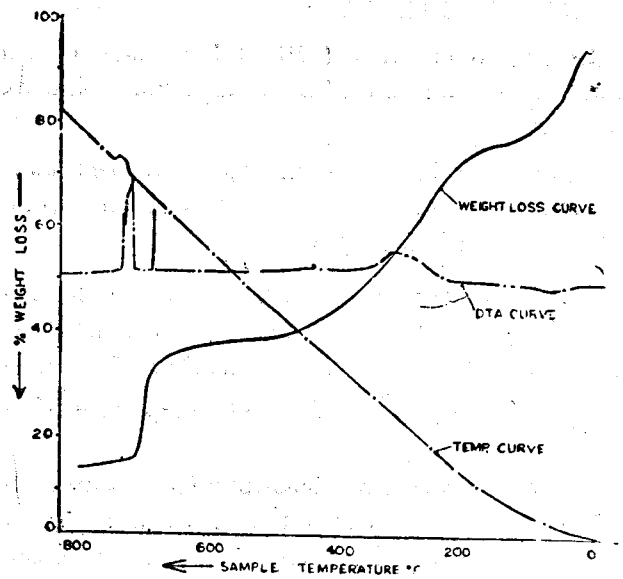

FIG. 2, TG & DTA Curve of Black Liquor Without Hemicellulose

liquor primarily due to diverse cellular ultra structure & varying chemical composition. Agricultural residues are characterized by high proportion of pentosans and silica. The result in Table—1 show that bagasse had pentosans almost equivalent to the amount of lignin. Similarly, cereal straws also contained higher proportion of pentosans. Hemicellulose are non-crystalline entity representing major proportion of total carbohydrates. Hemicelluloses contain mixture of low molecular weight pentosans & hexosans. In earlier studies, high molecular weight lignin fraction was one of the factor which influenced the vsiscosity of black llquors[6]. Not much of information is available on the role of dissolved hemicelluloses and also the lignin-carbohydrate complexes on black liquor properties. In the present investigations studies on behaviour of the black liquors after isolation of hemicelluloses were carried out.

Isolation of hemicelluloses :

The magnitude of dissolution and degradation of hemicelluloses to simple organic acids is largely influenced by the pulping condition employed. In chemical pulping where nearly 50% of the organic matter is dissolved, the resulting black liquor is usually rich in lignin followed by hemicelluloses and carbohydrate

degradation product.[3] Number of both physical & chemical methods are available for separation of hemicellulose from black liquors. However, the isolation of hemicelluloses by addition of methanol has become more common due to simplicity. Venter, et. al[3] have discussed in detail the method of precipitation of hemicelluloses from spent liquors. The hemicellulose is present in a solvated gel state and strongly associated with water. The association is destablized by addition of methanol and as a result the hemicellulose precipitates out from the black liquor. Similarly, the silica also gets precipitated due to destablization of electrical charges.

Table-2 shows the mass balance during isolation of hemicellulose & results indicate that 85 Kgs. of hemicellulose was separated per ton of spent liquor solids. Nearly 18 Kgs of lignin, 8 Kgs of silica and 4 kg. of sodium were associated with hemicellulose isolated. Although major proportion of carbohydrate is not chemically associated with lignin but some raw materials do contain significant proportion of lignin-Carbohydrate complexes (LCC). Generally, arabinose and galactose are associated with lignin. The cleavage of covalent bonds in LCC is often difficult[7]. Presence of nearly 15% of lignin in precipitated hemicellulose isolated after methanol addition clearly indicate the presence of significant proportion of LCC in bagasse black liquors.

Table-3 shows chemical properties of isolated hemicellulose. Calorific value (13.63 KJ/g) is on lower side as compared to calorific value of lignin (19.6 KJ/g) due to higher carbon contents in lignin which ranges from 39-46% as against 23-25% in hemicellulose fraction[8].

Chemical Properties of Black Liquors : The results in Table-4 show reduction in total dissolved solids from 11.0% to 9.98% w/w after separation of hemicellulose from the black liquor. There was also a change in total alkali which was reduced from 28% to 27% after the removal of hemicellulose from the black liquor which is reflected in the analysis of hemicellulose where total sodium is 4.2%. The major portion of silica i.e. upto 8% w/w is removed from the spent liquor alongwith. hemicellulose. The residual silica content in spent liquor was only 0.25% against original 1.73% which amounts to about 86% removal of silica. Thus desillication, an

TABLE—1

PROXIMATE CHEMICAL ANALYSIS OF AGRICULTURAL RESIDUES

Raw Material	Ash (%)	Silica (%)	Pentosan (%)	Lignin (%)
Bagasse	3.50	1.80	22.5	24.1
Rice Straw	18.40	11.80	19 3	13.6
Wheat Straw	7.20	3.20	19.2	18 5
Mixed Hardwood	0.89	0.03	16.0	27.7

All results expressed on O.D. raw material.

TABLE—2

MASS BALANCE SHOWING VARIOUS COMPONENTS IN PRECIPITATED HEMICELLULOSE

Particulars	Value*
Hemicellulose	85
Lignin	17.8
Sodium	4.2
Silica, as SiO_2	8 2

*Basis – Kgs/t spent liquor solids

TABLE—3

CHEMICAL AND THERMAL PROPERTIES OF HEMICELLULOSE PRECIPITATED FROM BLACK LIQUOR

Particulars	Value
Sodium, % w/w (as NaOH)	6 41
Silica, % w/w	7.1
Lignin, % w/w	15.5
Hemicellulose, % w/w	71.0
Calorific value, kJ/gm	13.67
Ignition temp. (Tig), °C	484
I.P.D.T., °C	373

TABLE—4
PROPERTIES OF BLACK LIQUOR AFTER ISOLATION OF HEMICELLULOSE

Component	Original B.L.	Black Liquor after isolation of hemicellulose
PH	12.30	12.31
Total dissolved solid ,% w/W	11.0	9.98
Residual Active Alkali as NaOH, % w/w	2.06	1.88
Total Alkali as NaOH,%w/w	28.0	27.0
Total Organics,% w/w	71.03	73.28
Lignin (by UV),% w/w	35.6	40.00
Hemicellulose, % w/w (by MeOH precipitation)	11.5	—
Degradation Products,%w/w	21.78	—
Silica as SiO_2, % w/w	1.73	0 25
BOD_5, g/l	26.5	20.9
COD (Cr), g/l	113 0	87.0
BOD_5 reduction, %		25
COD reduction. %		24

TABLE—5
MASS BALANCE SHOWING VARIOUS COMPONENTS IN BLACK LIQUOR*

Component	Original Black Liquor	Black Liquor after isolation of hemicellulose.
Total solids	963.0	873.0
Total Alkali as NaOH	270.0	260.0
Total Organics	684.0	611.0
Lignin	343 0	385 0
Hemicellulose (by MeOH Precipitation)	111.0	—
Degraded Product (By difference)	210.0	**
Silica as SiO_2	16.67	2.4
BOD_5 load	245.0	183 0
COD (Cr) load	1046.0	779.0

* Basis-kgs/tonne of pulp
** Not determined

important step in chemical recovery, is also accomplished alongwith hemicellulose isolation. Tne liquor after removal of hemicellulose and silica can be processed in conventional recovery systems. The higher proportion of carbohydrate residues & their degradation products lead to higher BOD values. The results in Table-4 show that there was a substantial reduction in BOD value (by about 25%) after removal of hemicellulose.

Mass balance during hemicellulose separation : Results of mass balance in Table-5 indicate that after separation of nearly 110 kgs of hemicelluloses and 14 kgs. of silica from black liquor, the lignin content was increased to 385 kgs/tonne of pulp as against original value of 343 kgs/tonne of pulp. With the removal of hemicellulose and silica and also lignin associated with hemicelluloses, the net dissolved solid contents decreased to 873 kgs from 963 kgs/tonne of pulp. As a result of removal ot hemicellulose the BOD and COD loads were reduced by about 25% and 24% respectively. The mass balance indicate that although the solids/tonne of pulp is reduced but the net heat available/tonne of pulp (see table 7) did not change substantially

Rheological Properties : Viscosity of concentrated black liquors has a profound influence on the efficiency of recovery system, evaporation section in particular. Spent liquor from agricultural residues, generally show high viscosities as compared to wood black liquors. Bagasse black liquor exhibits very high viscosity as compared to straws. The rheological properties of black liquors which are a colloidal solution of lignin & carbohydrate polymers is determined by the nature of these dissolved organic Polymer. Table-6 shows the viscosity of the two liquors as various solids concentration and temperatures. The data clearly shows that removal of hemicellulose resulted in substantial decreate in viscosity of the black liquors. If we compare the viscosity at 64% solids the iquor after, removal of hemicellulose showed a marked reduction in viscosity at temperatures upto nearly 104°C. The viscosity results clearly show that besides the molecular size of lignin macromolecules, the lignin carbohydrate complexes and dissolved hemicullulose also influence the viscosity of black liquors. However, this needs further investigations to confirm the role of carbohydrate-lignin complexes.

TABLE—6

RESULT OF VISCOSITY OF BLACK LIQUORS

Particulars	Original Black Liquors				Black Liquor after hemicellulose precipitation				
Total Solids % w/w	Viscosity, m. Pa. Sec.. at temparatures 82°C	93°C	104°C	115°C	Total Solids % w/w	Viscosity m. Pa. Sec. at Temperatures 82°C	93°C	104°C	115°C
30	10 6	8.6	7.3	*					
38	33.0	19.8	15.1	14.5	36	4.0	3 3	2.6	*
45	72.5	64.3	45 3	28.6	49	15.2	8 6	7.9	3 3
52	224 0	158 0	105 5	59.0					
64	1747.0	923.0	363.0	145.0	64	1318.0	290.0	198.0	154.0

* Viscosity could not be determined as liquor was boiling.

TABLE—7

COMPARATIVE THERMAL PROPERTIES/HEAT BALANCE OF BAGASSE BLACK LIQUOR

Particulars	Original Black Liquor	Black Liquor after isolation of hemicellulose
Lower Calorific Value, kJ/g*	14.78	16.07
Higher Calorific Value kJ/g **	20.80	21.94
Calorific Value GJ/T Pulp	14.2	13.9
Net reduction in heating value, %	—	2.1
Swelling Volume ratio (SVR) ml/gm	14.0	53.0
Ignition Temperature°C	705	711
IPDT, °C	490	497

* Calorimetric heat values
** Water and Ash free
** Higher Calorific Value KJ/g

Thermal Poperties : Table—7 show the various thermal properties of black liquors. The calorfic values indicate that despite removal of hemicellulose and subsequent reduction of organics by about 10% still there was an increase in calorific value, primarily due to higher proportion of lignin concentrations in black liquors after removal of hemicelluloses. If we look into the net heat losses due to reduction in solids/tonne of pulp, it is only a marginal i.e. about 2%. Swelling volume ratio (SVR) which is a semiquantitative measure of degree of pyrolysis, was extremely good for black liquor after removal of hemicelluloses. The increased SVR value might be attributed to increased plastifying action of polymers in absence of hemicelluloses having low plasticity. The IPDT and "Tig" values calculated from TG and DTA curves (Figures 1, 2, 3) are on higher side for black liquor after removal of hemicellulose due to absence of quicker burning of hemicelluloses which is observed in burning profile curves.

Proposed Scheme for separation and recovery of chemicals :-

Bagasse black liquors contain significantly higher proportion of dissolved hemicelluloses. The dissolved

hemicelluloses accounts as high as 30%[3] on total solids basis and about 30-40% of the total organic residues. The primary aim of burning the black liquor is to recover maximum amount of available heat energy. Hemicellulose fraction in black liquor is more or less a dead load in the system and the heat available from hemicellulose is relatively very low as compared to lignin. Besides the dead load hemicellulose also adversely affect the black liquor properties. In the present studies about 12% of hemicellulose was separated from black liquor and resulting black liquor had favourable properties and the Net heating valuc was not affected. The removal of hemicellulose should further facilitate in increasing the capacity of evaporators and also recovery furnaces. A route for new approach for separation and recovery of chemicals is illustrated in Fig. 4. Although the system incorporates additional stages of methanol addition and recovery of methanol but considering the advantages and also potential uses of isolated hemicelluloses it is worth while to consider this approach. Efforts on semi-pilot and pilot plant scale Will be needed for assessing the techno--economic viability.

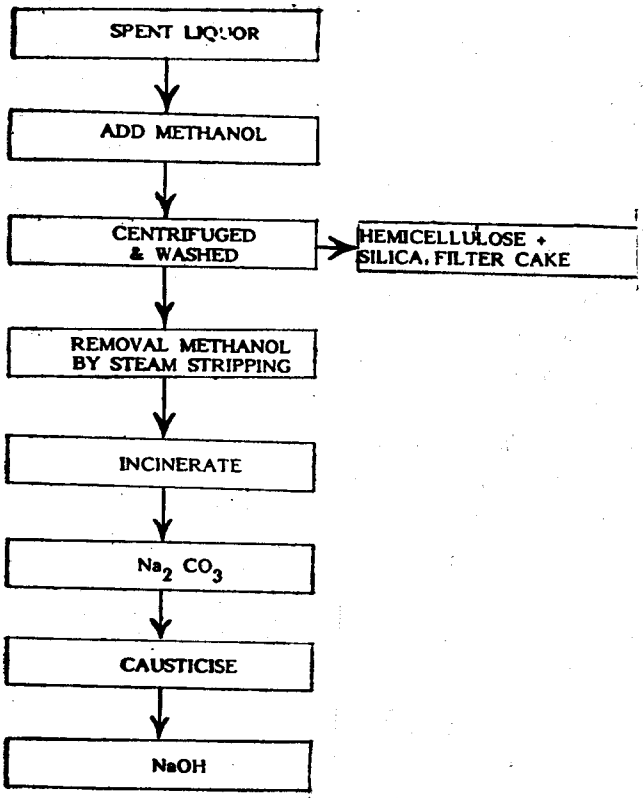

FIG. 4 : Proposed Route for Separation and Recovery of Chemicals from Spent Liquors.

CONCLUSION :

- Studies indicate that black liquors contain significant proportion of dissolved hemicelluloses.
- Removal of hemicelluloses improved the viscosity of black liquors and also burning properties.
- Desilication step is also accomplished in hemicellulose removal stage.

Considering advantages of disilication and improved liquor properties after hemicellulose removal, the new approach to chemical recovery after isolation of hemicellulose will have a promising potential.

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