Economics of Chemical Recovery Systems for Small Pulp Mills When Seen as End Effect of Recovery of Chemicals and Minimized Pollution

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ABSTRACT

Due to absence of chemical recovery system, small mills are loosing valuable chemicals and at the same time pollution problems are aggravated. Today with the stringent legislation to pollution control, these mills have to go either for chemical recovery system or treatment of effluents with heavily loaded organic and inorganic pollutants.

The present paper describes results of investigation on various organic constituents in spent liquors from pulping of agricultural residues and resulting pollution loads in terms of COD, BOD, etc. Studies conducted show that lignin constitutes nearly 50% of the total organic residues and it is expected that about 400-500 kg. of lignin/t pulp is going through spent liquor. Studies also include extent of bio-degradability of different black liquor components. It is well established that under normal conditions the lignin is a biologicallv refractory material and is difficult to degrade. For effluents containing such high proportion of refractory organics, the conventional effluent treatment methods may also involve high operationl costs.

The paper also deals with the economic benefits by going in for chemical recovery, whete chemicals are recovered and heat is generated from organic residues instead of perforcing the conventional treatment of spent liquors/effluents where neither chemicals are recovered nor useful organic residues are utilised. Findings clearly justify the benefits of process involving recovery of chemicals and at the same time utilising the organic residues as fuel.

During the last decade number of small mill based on agricultural residues have come up and today these mills are contributing over 30% to the total paper produced in the country. Due to absence of chemical recovery system, spent liquor generated in most of these mills is being drained and as a result valuable chemicals and useful organic residue are going as waste. As per an estimate a 30 tpd mill based on straw using 10% active alkali will be discharging about 1800 tons of caustic per anum and total value of caustic and energy potential lost annualy with black liquor as effluent is about 1.25 crores[1]. Considering several other mills of capacities near 30 tpd it is evident that the recurring loss faced by these mills would be enormous. Thus it becomes imperative to develop a technology which can recover valuable chemicals and at the same time useful organic residue is utilized.

Alternative approach, to overcome the pollution problem would be to have fulfledged treatment facilities for treatment of black liquors/effluents. Magnitude of the pollution in small mills is two to three times the total pollution load generated by a 100tpd mill[2]. Lignin. a bilogically refractory material, constitutes the main organic component and about 400-500 kgs of lignin per tonne of pulp is going through spent liquors[3]. It would be an enormous task to bring down the pollutional parameters like BOD, COD, color, etc. to a level of tolerance limit, by conventional treatment of effluents with highly loaded refractory organics. Various alternatives have been suggested by Gharekhan, etal[4] for treatment of effluent from small pulp mill.

Like chemical recovery system, treatment of effluents would also involve considerable capital and operational costs. Chemical recovery is productive in the sense the chemicals are recovered back and organic residues are utilized as fuel, while treatment is non-

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productive. In this context, it becomes imperative to evaluate critically economics of chemical recovery vis-a-vis effluent treatment system.

The present paper discusses the results of investigations on the pollutional loads due to various organic components of spent liquors and their biodegradability. The paper also covers the economic aspects of chemical recovery vis-a-vis effluent treatment.

EXPERIMENTAL

Raw Material: Rice straw was collected locally. The stalks were cut manually into 1—2" length. Bagasse was procured from a nearby mill in the form of bales. The bales were broken and soaked in water for overnight and then passed through a disc refiner at a high clearance to loosen the pith. The pith was separated by screening on the vibratory screen using 0.3 mm slot width screen. The pith free fibers were dried.

Pulping : The Pulping was carried out in the laboratory 25 L, tumbling digester. For rice straw 10% alkali was charged and 12% for bagasse. After pulping the spent liquor was collected by squeezing the pulp on a cloth. The pulp was washed and washings were also collected. In the second cooking cycle, the washing/black liquor were added to make up the bath ratio, which was kept at 1:6 A, constant H—factor was maintained for all pulping experiments.

Spent Liquor Analysis : Chemical properties of the spent liquors were determined according to TAPPI Standard method, T 625 ts—64.

Lignin Separation : Lignin was separated from the spent liquor by acidifying to pH 2.0 followed by centrifuging and washing till free from acid. Ash in lignin was also determined. The supernatant after lignin separation was collected for further analysis.

Determination of Pollutional Parameters : Various pollutional parameters, like BOD, COD, suspended solids and color of the effluents, were determined. The BOD and COD were determined by the method mentioned in the "Standard methods for the examination of water and waste water", 16th Edn.,APHA-AWWA-WPCF (N.Y.). The BOD and COD of lignin was measured after dissolving in 1N NaOH. The color of all the samples was measured at pH 7.6.

Lignin co-agulation with Alum : A known strength of alum solution was used for co-agulation of lignin at different pH levels of 5, 6 and 7 and residual colors were measured.

RESULTS AND DISCUSSION

Magnitude of Pollution in small Mills : Magnitude of the pollution would depend upon the raw materials used, pulping process employed and extent of recycling of black liquor. Table-1 shows the loads of various pollutional parameters like BOD, COD, SS, etc. in the mills of varying capacities. The volume of the black liquor generated also shows wide variation presumably due to different washing systems and varying amounts of water used in the dilution of the pulps. The volume of water used in the mill also shows wide variations. The resulting BOD, COD and SS loads in the final effluent show marked variations. It is clear from the data, collected from these mills, that there is a wide variation in the pollution loads when expressed on per tonne of the product.

Analysis of Black Liquors from Rice & Bagasse Spent liquors from two of the commonly used agricultural residues rice straw and bagasse were analysed in detail for lignin and other organics In both the cases a set of experiments involving recycling of a portion of the black liquor from first cooking were also conducted to see the increase in the total dissolved solids. Results are given in Table-2.

The total dissolved solids per tonne of pulp were 1.02 and 1.18 t, in bagasse and rice straw black liquors respectively. There was a substantial increase in the solids content when the liquor was recycled. The organic contents were on lower side for bagasse black liquor, persumably due to higher pulp yields and higher chemical dosage during pulping, compared to rice straw black liquor. The lignin content was on higher side for bagasse black liquors than rice straw black liquors. Other organics, which normally include organic acids, low molecular weight carbohydrates, etc. were on higher side for rice straw black liquor. Spent liquors from rice straw and bagasse differed substantially with respect to total organics and lignin contents.

Pollution Loads of Black Liquors and Organics : Black liquor contains three major components, as evidenced in the Table—1, namely inorganic component about 23-29%, lignin about 35 to 46% and remaining portion contains mostly organic acids derived from lignin and carbohydrate degradation. During pulping only part of the lignin becomes dissolved but major portion is solubilized as large colloidal macromolecules. Thus most of the lignin dissolved is in polymerised form to varying extent. It was observed by Pant, etal[3] that bagasse black liquor contained highly polymerized form of lignin compared to rice straw black liquor. Pollution loads in terms of COD and BOD, to a large extent, are influenced by the ratio of lignin to other orgnic components. In the present studies the pollution loads (BOD and COD) were estimated separately for black liquor, lignin isolated from black liquor and supernatant containing other organics after separation of lignin. The results are given in Table-3.

Table—1

POLLUTION LOADS IN SMALL MILLS*

Mill	Capacity t/day	Black Liquor m^3/t pulp	Effluent m^3/day	Black Liquor solids,%	COD, Kg/day	BOD,Kg/day	SS, kg/day	pH
1.	50	12	8000	1.4	19200	4800	24000	8.5-9.5
2.	30	7	6500	—	23900	3250	1170	7.4
3.	30	17	5000	4.0	20000–40000	5000–15000	2500–7500	6.5-7.5
4.	30	70	7000	4.0	21000	5950	5950	7
5.	15	12	568	—	445	136	80	6.3
6.	20	80	6100	3 0	19200	8200	11590	7-7.5
7.	20	8	1200	—	708	330	168	8.3

*Data based on the information collected from small mills.

—Data was not available.

Table—2

ANALYSIS OF BLACK LIQUORS

Particulars	Bagasse		Rice straw	
	Original	Recycled*	Original	Recycled*
Pulp yield, %	55	55	50	50
Raw materials, t/t of pulp	1.82	1.82	2.0	2.0
Alkali charge, %	12	12	10	10
Alkali charge, kg/t pulp	218	218	200	200
Black liquor, m^3/t, pulp	10.9	10.9	12	12
Total dissolved solids, kg/t, pulp	1020	1407	1183	1351
Total suspended solids, kg/t, pulp	4	13	19	20
Inorganics, %	27.9	29.4	22.8	26.2
Organics, %	72.1	70.6	77.2	73.8
Lignin, %	45.3	42.1	33.4	37.5
Lignin, kg/t, pulp (ash corrected)	463	592	395	507
Other organics, kg/t pulp.	273	447	518	492

*Portion of black liquor was recycled for next cooking cycle.

Table—3

RESULTS OF POLLUTION LOADS OF BLACK LIQUOR AND ORGANICS

	Particulars	Bagasse Original	Bagasse Recycled	Rice straw Original	Rice straw Recycled
Black Liquor	COD, kg/t pulp	1075	1396	1247	1347
	BOD, kg/t pulp	216	267	234	341
	COD/BOD	5.0	5.2	5.3	4.0
	Color, kg/t pulp (PCU)	1394	1817	1514	1896
Lignin separated	COD, kg/t pulp	530	785	628	639
	BOD, kg/t pulp	— was not	biodegradable	—	
	Color, kg/t pulp (PCU)	1283	1642	1444	1728
Supernatant free from lignin	COD, kg/t pulp	417	596	381	514
	BOD, kg/t pulp	197	244	247	—
	COD/BOD	2.1	2.4	1.5	2.0
	Color, kg/t pulp (PCU)	82	87	113	178

PCU—Platinum Cobalt Units.

Results show that COD and BOD values for bagasse black liquors were on lower side compared to rice straw black liquor due to lower proportion of organics. There was a drop in COD/BOD ratio for recycled spent liquor of rice straw and was presumably due to higher portion of other organic components which has led to increased BOD value.

Lignin separated from black liquor was dissolved in alkali and its BOD and COD values were measured. It was interesting to observe that the lignin totally was not degraded biologically. The COD values of lignin indicate that about 50% of COD value of the black liquors was due to lignin. Nearly 90% of the color in the black liquor was due to lignin which is further supported by lower color values of supernatants. Supernatants free from lignin show lower COD/BOD ratios compared to corresponding black liquors. This again confirms the fact that the resistance of lignin for biological degradation was responsible for higher COD/BOD ratios in black liquors. Despite removing the acid–insoluble lignin completely the supernatants still show some residual color around 6–10% of the initial color values. The residual color might be due to acid soluble low molecular weight lignin components.

These results clearly indicate that under similar conditions the lignin is completely a biologically refractory material and BOD values of black liquors are attributed to components other than lignin.

Removal of Lignin from Black Liquor: In the previous sections it has been established that over 90% color and nearly 50% of the COD values of spent liquor were due to the dissolved lignin. Lignin precipitated by acid treatment are normally gelatinous and would be difficult to remove due to slow settling. It was decided to remove the lignin by conventional alum-treatment method. Alum acts as coagulating as well as flocculating agent. During alum treatment pH levels 5, 6 and 7 were fixed. The results are given in Table–4. In the bagasse black liquor dosages of the alum were required compared to those for rice straw black liquor to bring down to the same pH level. The lignin in the bagasse black liquor was precipitated at around pH 7 with a color reduction around 90%, while in the case of straw black liquor at the same pH level it was difficult to precipitate the lignin. At pH 7 the color of straw black liquor was as high as 82% indicating inability of the lignin to precipitate. These results clearly indicate the inital pH of the liquor and colloidal stability of lignins will determine the requirement of the dosage of coagulant. The bagasse black liquor according to previous studies by Pant, etal[3] had higher molecular weight lignins and these high molecular weight fractions are colloidally unstable and very sensitive to pH changes. Slight reduction in pH of liquor tend to precipitate. It is difficult to precipitate the low molecular weight lignins.

Table—4

LIGNIN REMOVAL FROM BLACK LIQUORS

	Alum dosage kg/t pulp	pH	Resulting color kg/t pulp	Residual color %	Cost*/day Rs.	Cost*/yr. Rs.
Bagasse Black liquor Initial color-1394 kg/t	508	5	30	2.2	15240	4572000
	390	6	111	8.0	11700	3510000
	277	7	165	11.8	8310	2493000
Rice straw Black liquor Initial color 1514 kg/t	306	5	195	12.9	9180	2754000
	198	6	1194	78.9	5940	1782000
	57	7	1235	81.6	1710	513000

*Cost of alum—Rs.1/kg, and the costs calculated are for 30 tpd, mill, with 300 working days.

For about 80% color removal, by separating lignin, alum dosage of about 277 kg/t pulp in case of bagasse at pH 7 and about 306 kg/t pulp in case of rice straw at pH 7 would be required. Cost of alum dosage for 80% color removal would be around Rs. 25,00,000/year. Color removal will be accompanied by COD removal to the extent of around 50%. From the pollution load studies it is clear that removal of lignin will not help in reducing the BOD load.

Economics of Pollution Treatment vis–a–vis Chemical Recovery System : Economics involved for treating effluents from small mills have been worked out by different technical experts. Accordeng to Sadawarte[5] the cost of treatment, varies from Rs. 10 lakh to Rs. 37 lakh for the mill capacities from 20 to 50 tpd, to have a final effluent suitable for on–land discharge for irrigational purpose. For discharge into in–land surface water the cost of treatment varies from Rs.54 lakhs for 20 to 50 tpd, size mills. Further it has been pointed out that high alkali content will be the limiting factor for on–land discharge of effluents for irrigational purpose, in which case the effluent will be required to be neutralized with acid or gypsum salts.

Based on the alum dosage required for removal of lignin and the costs involved for BOD removl (Appendix-I) the total operational costs for removal of lignin and BOD to a tolerence limit would workout in the range of Rs. 4500000/year for a typical 30 tpd mill based on bagasse and rice straw, besides the capital involved in treatment facilities. The recurring losses due to caustic and organic mass lost through spent liquors (Appendix-II) would be around Rs,2 Crores/year. Even after deducting the operational cost of Rs.1.2 Crores/year in chemical recovery, the net savings would be around 0.8 Crores/year. In the case of pollution treatment, though the operational costs are on lower side, but the whole system would be non–productive in the sense neither cooking chemicals are recoverd nor the dissolved biomass is utilized. In absence of chemical recovery system, besides the recurring loss of 2.0 Crores/year, additional burden of recurring expenditure towards the operationl costs involved in effluent treatment, has to be borne. Thus considering the recurring expenditure, in the long term, installation of the chemical recovery would be beneficial both in terms of economics and minimized pollution.

CONCLUSIONS

1. Analysis of pollution loads by black liquor and its organic components clearly reveal that over 90% of color and 50% of COD in black liquor is attributed to lignin.

2. Components other than lignin were bio-degradable and BOD load in black liquors was essentially due to these components.

3. For removal of BOD., COD and color, it may be necessary to isolate lignin by precipitation using coagulants before going for biological treatment methods.

4. Based on the economics worked out for effluent treatments vis-a-vis chemical recovery system, it is revealed, chemical recovery should be the only alternative.

5. When seen as end effect of recovery of chemicals, and minimized pollution problems, case for installation of chemical recovery system becomes strong.

APPENDIX—1

OPERATIONAL COSTS FOR SPENT LIQUOR TREATMENT

Capacity — 30 tpd (Unbleached pulp)

Tolerence limit of BOD — 50 mg/1 (0.05 kg/m^3)

Cost of treatment — Rs.1/kg of BOD (6)

Bagasse Black Liquor :

Total black liquor — 10.9 m^3/t pulp

Total BOD load — 216 kg/t pulp

BOD, after treatment — 0.05 kg/m^3 i.e. 0.545 kg/t pulp

Total BOD, required to be removed — 216-0.545 = 215.46 kg/t pulp

Cost of treatment at Rs. 1/kg BOD — Rs. 1215/t pulp=Rs. 6450/day

Recurring expenditure — Rs. 1935000*/yr.

Rice Straw Black Liquor :

For rice straw which had lower pulp yields compared to bagasse the cost of treatment would be around *Rs. 2101095*/year.*

*For calculation of cost per year, 300 working days/year has been taken.

APPENDIX-II

ECONOMICS OF CHEMICAL RECOVERY

1) **Recurring losses due to absence of Recovery System.**

Capacity — 30 tpd (Rice straw based)
Alkali charge — 10%
Pulp yield — 40% (Unbleached)

300 working days/year.

a) Total alkali losses through Spent liquors — 2250 tons/year.
Cost of the alkali lost—Rs. 13500000/year (Rs. 6000/t of caustic)

b) Total organic mass lost through spent liquors (5% Ash in straw)—41.25 tonnes.

Calorific value of straw spent liquor—3200 k cal/kg

Organic mass equivalent to the coal having calorific value of 4500 k. cal/kg—30t (approx).

Cost of the energy potential lost–Rs. 6750000/year

(Assuming the cost of coal—about Rs. 750/t).

c) Net recurring loss due to caustic and organic mass

as energy potential=a+b=*Rs.2 0 Crores/year (approx).*

2) **Operational cost in Chemical Recovery :**

Based on the estimation by Kulkarni, etal[7] and considering cost of chemicals, utilities (water, power, coal, etc.) and operational and maintenance, prevailing today, the operational cost in conventional recovery for a typical 30 tpd mill will be around Rs. 40,000/day.

Net operational cost—*Rs. 1.2 Crores/year*

Net savings by going for chemical recovery will be (Rs. 2.0—1.2)=*0.8 Crore/year.*

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