By–Products from Non–Wood Fibre Pulping for Industrial Applications

*Kulkarni A G , *Jain R.K., *Gupta Abha , *Bisht Mamta.

ABSTRACT

In the last two decades, there has been a remarkable increase in utilization of nonwood fibres such as cereal straws and bagasse. Today the installed capacity of mills based on these raw materials is about 0 9 million tonnes per year. The seasonal availability and the processes employed limits the size of the mills. More than 200 mills are operating throughout the country and none of which have any system for recovery of chemicals or useful by–products from dissolved residues in spent pulping liquor. Lignin, hemicelluloses and silica are three important recoverable by–products useful for various industrial applications. From a typical 30 tonne per day pulp mill, 9 tonnes of lignin, 5 tonnes of hemicelluloses and 1.5 tonnes of silica/per day can be recovered It is also possible to recover the cooking chemical in the form of sodium sulphate and almost 10 tonnes of 90% pure sodium sulphate can be regenerated from the inorganic residues. CPPRI has initiated this integrated approach to develop methods and processes for recovery of these valuable by–products. The present paper highlights various routes proposed for recovery of the by–products and their end applications.

Introduction :

India is one of the leading countries in utilization of nonwood fibres for pulp & paper manufacture. In the last two decades there has been notable increase in the utilization of nonwood fibres. There are more than 200 units having capacities less than 30 tonnes per day. Due to capital intensive nature, these mills can not afford to have any chemical recovery and/or treatment system for spent liquors. Absence of chemical recovery has resulted in severe pollution problem and mills are facing problems in complying with environmental regulations. These mills are making valuable contribution in the paper industry by way of conserving the forest resources. Although the capacity of these mills does not permit the installation of any kind of recovery system, however by recovering the dissolved organic and inorganic substances and converting them into a useful industrial by-products, these mills can become economically viable in the long term These mills continue to survive in absence of chemical recovery system, primarily due to the fiscal incentives. Instead of decomposing the low molecular weight organic residues into carbondioxide & water by biological treatment by putting energy, it is worth while to recover the main organic residues like lignin, hemicellulose before discharging effluent.

Central Pulp & Paper Research Institute is actively engaged in identification and development of processes for recovery of various organic & inorganic by-products from the wastes generated in these small mills. Some potential areas were identified by Kulkarni et al [1, 2]. Removal of hemicelluloses from spent liquors has also been considered as practical proposition for incremental capacity in chemical recovery[3]. Venter, etal[3] have also discussed about the advantages of reclaimation of hemicelluloses.

*Central Pulp and Paper Research Institute,
P.O. Box No 174
Saharanpur–247001 (U.P.) INDIA

Looking into the practical problems these small mills are facing and to ensure their survival with better environment, recovery of lignin, hemicelluloses, silica and sodium sulphate is a viable proposal. Recovery and utilization of these resources will also make entire process a cost effective one.

Result & Discussions :

By-products from spent liquors :

Spent pulping liquors contain about 70% organic residues and 30% inorganic residues Nearly 50% of the organic residues is accounted by the high molecular weight lignin fractions Small mills which can not afford any chemical recovery or treatment systems, the recovery of by products is a viable proposition. Depending on the size, tvpe of pulping process and raw materials employed, different routes have been conceived and discussed below.

Small mills based on straw :

Rice straw is the most widely used among the cereal straws and nearly 100 mills are employing straw as their main raw material. The straws are characterized by high silica contents and depending on the region, the ash content varies from 6-18%. Due to inherent problems and size of the mill, it becomes economically un-viable to install a recovery system On the other hand, treatment of black liquor to comply with environmental regulations is also a non-productive approach The third route to recover valuable organic & inorganic residues and to use them elsewhere should make the entire process a cost effective one. The route-1 proposed is intended for straw based mills. Lignin and Na_2SO_4 are recovered by acid precipitation using H_2SO_4 About 300 kgs of crude lignin and about 400 kgs of Na_2SO_4 per tonne of pulp can be recovered.

Lignin which is difficult to filter has been made easily filtrable by using organic additives. After recovery of lignin, the Na_2SO_4 is recovered by evaporation and crystallization. Recovered Na_2SO_4 has a purity of about 90% and could become a useful substitute for salt cake in integrated kraft mills. Table-1 gives mass balance of various by products and pollutional parameters for a normal fibre based pulp mill.

Table-2 indicates the tolerance limits of the effluent and also the discharge characterisation of the effluent before & after by-product recovery. The filtrate almost free from 'Na' and lignin, should become ideal for on land discharge and irrigation, without any further treatment.

Assuming the operating cost of effluent treatment and recurring expenditure involved in by-product recovery, at par, the accruing financial benefits work out to be around Rs. 24 million which works out to be a reduction in the cost of manufacturing by about Rs. 1400 per tonne of pulp as shown in Annex-1.

Annex-1

Preliminary Indications of Economic Benefits :

a) Operating cost for recovery of lignin — @ Rs. 400/tp

b) Operating cost for recovery of Na_2SO_4 — @ Rs. 500/tp

Recovered lignin — 350 kg/tp

—Cost of recovered lignin (equivalent to coal) @ 1500/tp — Rs 525/annum

—Recovered Na_2SO_4 — 383 kgs/tp

Cost of recovered Na_2SO_4 @ 6000/t Rs. 2300/annum

c) Operating cost for effluent treatment Rs. 600/tp. @ 2 Rs/kg–50% COD removal)

. Net accuring benefit before adding the operation cost in effluent treatment — Rs. 18 million.

. Net accuring benefit after adding the operation cost in effluent treatment—Rs 24 million.

—Recurring loss without by-product recovery – @ Rs. 3800/tp

—Recurring loss with by-product recovery – @ Rs. 2400/tp

Thus, cost reduction per tonne pulp –@Rs 1400/tp

TABLE—1

Mass balance of recovered by products & pollutional parameters

State	Lignin	Hemicellulose	SiO_2	Na_2SO_4	BOD	COD
Black Liquor	343	185	17	490	240	1050
After hemicellulose removal	318	10	2.2	467	183	850
After lignin removal	18	10	0.2	443	175	350
After sodium sulphate removal	18	10	0.2	40.0	175	350

All values expressed as kgs per tonne bone dry pulp.

TABLE—2

Tolerance limits and discharge characteristics of effluent for land disposal/irrigation

Particulars+	Tolerance limit	Without by-product	With by-product recovery
Dissolved solids, mg/l	2100	5000	1750
Sulphates, mg/l as SO_4^{2-})	1000	N A.	260
Sodium (max)*, mg/l	1260	800	126
BOD, level for** land irrigation kg/hectare/day	225	240	197

+BIS-2490 (Part-I) 1981.

N.A –Not applicable

*Maximum limit 60% of dissolved solids.

**Land requirement-4.3–5.3 hectare/1000m³ effluent.

TABLE—3

Slaking results of final lime products

Fuel	Calcination %	% gas replaced	slaking time, min.	Temp°C Rise	Max.
Acid pptd. lignin	97.1	100	1.12	13 2	103.2
Case I	98 2	0	1.02	13.5	103 5

The coming years will notice an increased use of bagasse as a major fibrous raw material for pulp & paper making. Bagasse contain more than 22% hemicelluloses & major portion of which is dissolved during pulping. The resultant black liquor contains about 20% of the hemicelluloses, with high degree of polymerization and can be easily, reclaimed. Hemicelluloses with their low calorific value, 13.6 kJ/kg which is low in comparison with lignin which is almost '19.6 kJ/kg'. Thus excess amount of hemicelluloses going with black liquor is a dead load in recovery boiler and this dead load can be avoided by reclaiming hemicelluloses from the black liquor. The proposed route is illustrated in Fig. 2 which is similar to the Route -1, except with an additional stage of hemicelluloses recovery by methanol addition. This route is more ideal for integrated mills with recovery by reclaiming the hemicellulose, the mills can increase the capacity of their recovery boiler with increased overall thermal efficiency. This route might become expensive for small mills.

By-products from spent pulping liquors & their Industrial applications :

Utilization of lignin for various industrial application :

The crude lignin separated from spent pulping liquor may require further purification & modification, to use them as effective industrially useful by-product depending on their end application. The various application to which lignin can be put, may be broadly classified in to three classes.

- Physical utilization
- Chemical utilization
- As fuel in boiler and lime kiln.

Physical utilization—Lignin and its derivatives for various industrial application includes :

a) As an Industrial dispersants :

The use of lignin derivatives as grinding aids in cement and concrete industries represent a major outlet. These aids are often used to grind the clinker and to small extent, in the wet initial grinding. The lignins are found to be highly effective dispersants in wet grinding operation. Other major industries included are ceramic, dye, insecticides, rubber, cleaning agents manufacturing & oil well drilling [4].

FIG- 1 ROUTE-1 FOR SMALL STRAW BASED MILLS (Below -30 tpd capacity)

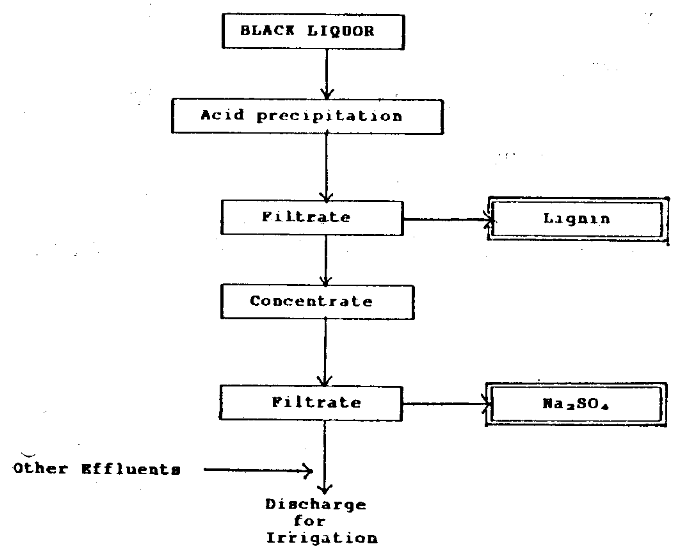
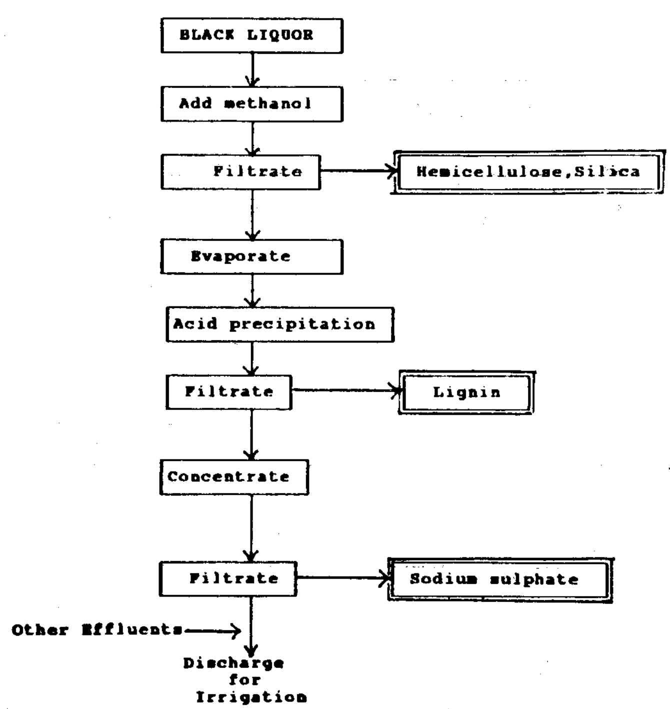


FIG-2 ROUTE-2 FOR BAGASSE BASED MILLS



B) Emulsifiers & stabilizers !

Lignin emulsifiers are quite competitive with other commercial emulsifiers stabilizing oil in water emulsions.

c) Binders and adhesives :

Lignin specially recovered from agro-residues black liquors e g. bagasse is found to be highly reactive than hardwood or soft wood lignins towards formaldehyde under alkali catalysed conditions. Traditional type of cold-setting wood adhesives and fast setting exterior grade wood adhesive has been successfully prepared from soda bagasse lignin [5].

d) Utilization of lignin gels for agricultural purposes :

The lignin gels are characterized by strong water retention capacity & the cross linked gels have now been commercially manufactured and when added to soil, the capacity of water retention of soil is improved.

2. Chemical utilization of lignin[3] :

Besides physical util zation discussed above, raw lignin constituents are abundant source of phenolic compounds which are extensively used in polymer industries. With the thermal degradation of raw lignin employing hydrocracking technique at temperatures around 375°C, phenols & cresols are obtained. The mixture of phenols upto 25% yield was obtained and these have been extensively used in the manufacture of adhesive. Considering the present scarcity of petroleum products the utilization of lignin for chemical purposes should give an value added advantage to recovered lignin.

In the long run the lignin from the small pulp & paper mills could be a replenishable source and undoubtedly can become an essential source of organic chemicals.

3. Utilization of lignin as fuel :

In lime kiln precipitated lignin after drying in the form of powder can be satisfactorily burnt in a lime kiln either on its own or in conjunction with conventional fuel ie coal or natural gas. The lime produced with lignin as fuel were equally as reactive in slaking as these produced by conventional fuel firing. There appears to be a small increment of fuel savings or through put increase possible upon conversion from natural gas to lignin. Slaking results of final lime produced where lignin has been used as fuel in place of natural gas are shown in Table–3.

Utilization of hemicelluloses :

Chemical analysis of precipitated hemicelluloses is shown in Table–4. Hemicelluloses recovered from nonwood fibre pulping spent liquors has been successfully used for various industrial applications.

TABLE—4
Chemical Analysis of precipitated Hemicellulose

Particulars	Values, kg/tp.
Hemicellulose,	135.0
Lignin	23.0
Sodium	7.2
Silica	14 4

Hemicellulose as a binder for char coal/coal[6] :

Hemicellulose has been proved to be a b tter binder for making of charcoal/coal briquettes. The compression strength of charcoal briquettes bonded with hemicelluloses were similar or better than those of briquettes bonded with a commercial starch binder.

Hemicellulose as surface sizer (wet end additive)[7] :

Use of hemicellulose has been successfully tried for the surface sizing of test liner and fluting manufactured from recycled kraft paper and also for surface sizing of both corrugated medium and liner board. The results were comparable with commercial starch surface sizes The use of bagasse hemicellulose as a corrugated board adhesive has also been studied. Currently, strength results obtained so far, under laboratory conditions, are extremely promising, work is currently aimed at improving its gel characteristics.

Conclusions :

1. Looking in to the limitation of the small mills and the regulatory measures for compliance with environmental standards by product recovery should help these mills in reducing the manufacturing costs while fulfilling the statutory environmental regulations to a greater extent.

2. The recovery of sodium sulphate and its use in other pulp & paper mills with recovery system and utilization of recovered lignin is an indirect approach of recovery of chemicals.

References :

1. Jain, R K; Gupta Abha, Kulkarni, A.G; and Pant, R; IPPTA Vol 2 No.3, Sept. 1990.

2. Kulkarni, A.G; Mathur, R.M; Gupta Abha & Pant, R; IPPTA, 24 (3) Sept, 1987.

3. Venter. J.S.M., Vander Klashorst, G.H, Tappi 72 (3), 1989.

4. Sarkanen, K.V, Lignins–occurance, Formation Structure and Reactions (K.V. Sarkanen and C. H. Ludwig Eds), Wiley Inter science, New york, 1971, CH20 P. 845—854.

5. Vander Klashorst, G. H, and Venter, J S.M, IS-WPC, Paris, Proceeding, Vol II, P. 385–390(1987).

6. R. Chardson, B, Watkinson, A.P and Barr, P.V, Tappi, 73 (12), 1990.

7. Vander Klashorst, G H., and Venter, J S.M, Holzforschung, 40 (6) : 375 (1986).

8. Vander Klashorst, G.H, and Venter, J.S.M, Appita, 40 (4) : 279 (1987).