BIOLOGICAL AND THERMAL PROCESSES FOR WASTE UPGRADATION AND REUSE IN PAPER INDUSTRY

- Veeramani, H.*

ABSTRACT

The major current sources of waste generation in a mini paper mill based on straws/bagasse include raw material cleaning, pulping (black liquor) and bleach plant. In a well operated large mill, the present practice leads to the generation of bleach plant effluents besides lime sludge disposed as a solid waste. This paper reviews alternate schemes for the recovery of chemical and energy from mini mill black liquors, integrated schemes for the treatment, upgradation and recycle of mill waste waters and calcination of lime mud for reuse in causticization. Elimination/reduction of waste generation would also improve the over-all economy of paper mill operations.

1. INTRODUCTION

Paper industry generates a significant quantity of wastes at various stages of production during large scale as well as small/mini-scale mill operations. The latter category of mills account for about one-fourth of the total estimated annual production of about 15 lakh tons of paper; the balance is made by the mills in the medium/large scale sector.

The nature and quantity of waste materials produced are determined mainly by the scale of mill operations, grade of paper or board, the cellulosic raw materials used as digester furnish for producing pulp and mill operating practices. The various pulping methods adopted strive to isolate the useful fiber portion from the non-fibrous constituents of the digester furnish. This objective is achieved by selective pretreatment steps prior to pulping as well as post cleaning steps to eliminate dirt, sand and shives from the pulp before making paper.

* Hindustan Dorr Oliver Limited, Bombay.

The various raw materials commonly available and selected for paper making in this country have specific waste generation implications and can be traced to certain associated characteristic of each fibrous species. Besides, certain class of materials like agricultural residues (rice/wheat straws) are currently used mainly by mills in the small/mini-scale sector owing to their location in the proximity of the fiber sources.

This presentation identifies the sources of waste generation during the various stages of operation in paper/board production. Remedial measures adopted by the mills to reduce the quantities of wastes generated as well as reuse schemes for waste utilisation are high-lighted.

Newer technologies available for waste utilisation and conservation of the resources are also discussed in the context of some typical requirements of paper mills. Recent advances are discussed pertaining to the following specific aspects relevant to the over-all economy of paper mills in both the small and large scale sectors.

a) System for recovery of caustic soda from black liquor discarded as an effluent by mini-paper mills.

b) Waste water generation and treatment by stream seggregation and recycling of the upgraded treated waters.

c) Reuse potentials for lime mud disposed as a solid waste by the larger paper mills.

2. SOURCES OF WASTE GENERATION

Solid or liquid wastes are generated at each stage of paper production besides the release of air-borne particulate matter in certain sections of the mill

The main mill operations consists of raw material preparation pulping, bleaching, chemical recovery and paper making. Various off-site facilities like power generation, cooling water and utilities are excluded from the scope of this paper.

RAW MATERIAL PREPARATION

All the fibrous raw materials require specific pre-treatment to remove the extraneous non-fibrous portions prior to pulping.This preparatory stage is rather elaborate especially while handling bagasse and straws for pulping.

Good cleaning of straws and bagasse prior to pulping can increase digester through-put and pulp yield, reduce consumption of alkali and bleach chemicals and improve pulp quality. Removal of extraneous mud and dirt will also reduce the concentration of silica in black liquor.

The pith content of bagasse constituting 30-35 % of crude bagasse must be removed for obtaining relatively clean bagasse rind fiber for pulping. This is accomplished by a combination of moist/wet/dry mechanical methods of pith removal. Some useful fiber is invariably lost in considerable quantity by these methods. Pith generated as a waste would account for 15-40 % depending upon the extent of depithing and the desired upgradation of bagasse fiber necessary for the grade of paper. Bagasse pith accumulating as a solid waste is utilised as fuel for boilers.

In the case of straws and grasses, it is necessary to remove chaff, grain, nodes and extraneous dirt and soil. The extent of cleaning necessary will be partial (usually dry) for making semi-chemical or coarse grade board pulp. A two stage dry and wet cleaning procedure will be necessary to make straw suitable for fine quality bleached pulp production. Straw cleaning operations can result in 10-25 % of waste generation. These wastes can be best utilised as a fuel in multi-fuel fired boilers.

The preparatory step for bamboo includes washing of culms prior to chipping or washing of the chips mainly for the removal of extraneous dirt and mud. The chipper house operations will produce bamboo dust similar to chipping woods.

PULPING/BLEACHING

Pulp mill operations (pulping - washing - bleaching) generate several waste water streams. These consist mainly of screen rejects from pulp cleaning and effluents discharged from chlorination, caustic extraction and hypochlorite bleaching stages. Small/mini-mills also discharge the entire black liquors as a waste stream and is a matter of serious concern since a large quantity of valuable caustic soda is lost in its once-through use for pulping.

CHEMICAL RECOVERY

An efficient chemical recovery system should ideally work with weak black liquor as the input and regenerated white liquor as the output stream for reuse in pulping. However, with bamboo as the conventional raw material for paper-making chemical recovery systems have been operating in the country with once-through use of lime for causticization of the green liquor. Lime mud with a high silica content (10-15 %) is not suitable for reburning and is discarded as a solid waste accumulating on adjoining land. This practice has continued even though several mills have replaced bamboo substantially (upto 75-80 percent) by mixed hardwoods. The cost of purchased lime has increased considerably over the years to about Rs. 750-800 per ton at many locations and the quality of lime has also seriously deteriorated. The performance of the causticization section is affected and a greater quantity of lime mud is generated and disposed as solid waste. Regeneration of white liquor represents a significant share of the final recovered chemical cost and a techno-econoic appraisal of lime mud reburning system is relevant for the prevailing high costs of operation, fuel and supplies.

Mini-paper mills do not have chemical recovery operations and the recovery of caustic soda from black liquor reuse in pulping is generally regarded as an uneconomical proposition. A mill based on straw (capacity - 30 TPD) using 10 % active alkali (as NaOH) with pulp yield of 45 % will be discharging spent caustic equivalent to about 1800 tons per annum. Potential energy loss represented by the calorific value of black liquor solids can be shown to be equivalent to about 6500 tons per annum of coal. The total value of caustic and energy potential lost annually with black liquor as effluent is about Rs. 1.25 crores (assuming Rs. 5000 per ton for caustic and Rs. 750 per ton of average coal of calorific value 4200 Kcal/Kg). This represents a major recurring expense besides accounting for 75-80 per cent of the total pollution load (BOD) released by the mill as waste waters requiring treatment.

Particulate emissions with recovery boiler stack gases consisting mainly of sodium carbonate have been effectively curtailed by the installation of electrostatic precipitators and/or venturi scrubbers. Mechanical cleaning of the tubes of the first few effects of the evaporation plant contributes to periodical release of the siliceous scale deposits as solid residues.

PAPER MAKING

Paper machine operation leads to a large volume of white water as a waste stream and consists mainly of fiber fines and filler material. Several mills have implemented in plant schemes for their recovery by installing disc/flotation save-all and settlers and the recovered fiber generally used as back-liners in board making. These mills have also been able to reuse the clarified water and achieved substantial savings in fresh water demand by efficient recycling. With more mills adopting fiber recovery and water recycling, paper machine operation is no longerregarded as a major source of waste water generation.

Thus, the major sources of waste generation currently identified for a mini-mill based on bagasse/straws include raw material cleaning, pulping (black liquor) and bleach plant. In a well operated large mill, the major sources include wastewaters from bleach plant and lime mud from causticizers.

3. MINI-MILL BLACK LIQUOR - CHEMICAL/ENERGY RECOVERY

There are currently two alternatives for processing the black liquors from the mini-paper plants based on straws and bagasse.The first method will be the direct adoption of a scaled down version of a conventional three-stage system with multiple effect evaporation, recovery boiler and causticization for the regeneration of caustic. An alternative strategy would involve the development of appropriate technology to establish the techno-economic viability of new routes such as 'DARS' which also would involve a three-stage processing consisting of evaporation, combustion and hydrolysis/leaching for the recovery of alkali.

There are several apprehensions impeding a proper appraisal of the techno-economic viability of a chemical recovery system and some of the issues pending to be resolved relevant to mini-mill operations are listed below:

a) Optimum size of the mill for an economical chemical recovery system.
b) Improvements in pulp mill operations - pulping and brown stock washing to increase the concentration of weak black liquor to reduce evaporation load.
c) Viscous nature of straw and bagasse black liquors tending to limit maximum concentration to 35-40 % with multiple effect evaporators.
d) Adverse effects of silica in black liquor during processing.
e) Low energy potential of black liquor solids and needs for auxiliary fuel during combustion.
f) Need for compact, low cost system.

Several of these limitations are easily overcome by incorporating some of the recent technological developments and innovations and the experiences oif operating mini-mills.

Several of these limitations are easily overcome by incorporating some of the recent technological developments and innovations and the experiences of operating mini-mills.

DARS - Direct Alkali Recovery System, is a potential alternative recovery scheme for paper mills based on soda pulping process and it is not suitable for kraft pulp mills. The process would involve combustion of semi-concentrated soda black liquor admixed with ferric oxide (hematitie) in a fluidised bed boiler. The sodium ferrite granules formed is then hydrolysed for the recovery of sodium hydroxide and regeneration of ferric oxide for recycle to the fluid bed reactor. Unlike conventional recovery plants, DARS would eliminate smelt handling and lime mud circuit for regeneration of white liquor from black liquor. The DARS flowsheet is based on the following combustion and hydrolysis reactions:

Combustion

$$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2$$

$$BLS + Fe_2O_3 = Na_2Fe_2O_4 + CO_2 + H_2O$$

Hydrolysis

$$Na_2Fe_2O_4 + H_2O = 2NaOH + Fe_2O_3$$

$$\text{Over-all : BLS} = 2NaOH + CO_2\text{(stack gas)}$$

Black liquor solids contain residual NaOH and Na_2CO_3 and sodium salts of lignin and carbohydrate degradation products. Sodium in black liquor solids will combine with ferric oxide to give the granular intermediate - sodium ferrite.

The stoichiometry of the DARS reactions and the feasibility of the flowsheet for handling straw and bamboo soda black liquors have been studied by scientists at CPPRI Dehradun(1). A commercial DARS plant is in operation at APPM, Burnie, Tasmania handling black liquor from soda - AQ pulping and Dorr Oliver has supplied the fluidised bed reactor for this project(2).

The concentration of weak black liquor discharged by a majority of the operating mini-mills is rather low (2-4 %) and chemical recovery schemes as discussed above would be impractical. The high concentration of biodegradable constituents suggests an alternative possibility of recovering the biochemical energy potential as biogas by anaerobic treatment. A recent paper by the author high-lights the tangible benefits of anaerobic treatment in a fluidised bed Door Oliver ANITRON biosystem with energy recovery as biogas for a 25 TPD paper mill based on bagasse (3).

4. WASTE WATER TREATMENT - UPGRADATION - RECYCLE

Aqueous effluents discharged by paper mills show considerable variation in quantity and characteristics. These are dependent upon product grades, mill capacity, fiber types, pulping/bleaching processes, operating mill practices and availability of water. All wastewater

streams from various mill operations are generally combined before treatment. The regulatory stipulations have made it mandatory to curtail the load of pollutants and regulate the quality of the effluent finally discharged by the mills.

A conventional effluent treatment scheme adopted by several mills consists of primary clarification for the removal of grits fiber and other suspended matter and secondary biological treatment by activated sludge or aerated lagoons to reduce the BOD levels before discharge. The secondary effluent is generally coloured and has an appreciable concentration of refractory organics lignins which contribute to high COD values.

The problems of residual colour and high COD of secondary treated effluent can be traced to the alkali extraction effluent from bleach plant and black liquor discharged by the mini mills. The colour is caused by polymeric fragments of dissolved lignin compounds and these remain largely undergraded in conventional anaerobic/aerobic treatment systems. A bench scale study reports colour reduction of alkaline kraft bleach plant effluent by the wood degrading white rot fungi capable of complete degradation of the native lignins, modified kraft lignins and chlorlignins. A rotating biological contactor has been found suitable to provide the necessary metabolic and physiological requirements. The rotating discs provide a surface for growth and mycelial mat formation while mixing and contacting the effluent with fungus. Colour reductions of upto 80 % have been achieved in the laboratory batch reactors. This invention has been named MyCoR (Mycelial Colour Removal) process - jointly developed by U.S. Forest Products Laboratory, Madison and North Carolina State University, Releigh(4).

Other conventional physico-chemical treatments for colour and COD removal are based on principles of precipitation, adosorption or chemical oxidation besides new membrane separation processes based on ultrafiltration. Colour reduction studies in various mill laboratories and academic institutions have used

additives like lime, alum, flyash, clay, activated carbon and commercial polyelectrolytes and reported varying degrees of effectiveness for reducing colour.

Thus, advanced wastewater treatment techniques also known as tertiary treatment, must be designed to remove the residual pollutants after conventional secondary treatment and achieve a better effluent quality. These methods have been increasingly adopted globally for wastewater reclamation. Treatment technology and methodologies are available today to achieve any desired level of upgradation of water quality by a judicious selection of an appropriate combination of unit operations and processes - adsorption, clarification, precipitation, filtration, ion exchange, ultrafiltration/reverse osmosis, chlorination,etc It is also necessary that the cost of the reclaimed water is competitive to justify the investment in the add-on facility and eliminate redundant steps in the treatment scheme while ensuring the removal of all known/unknown contaminants.

An optimum treatment plant can be designed for achieving maximum reuse potential and the final treated effluent characteristics would conform to the state pollution board limits. This can be effectively accomplished by segregation of the various wastewater streams and selecting treatment steps for the removal of specific pollutants. In this manner, the dual objectives of water reclamation and effluent treatment can be satisfactorily accomplished for handling the wastewater streams generated in the paper mill.

5. LIME MUD CALCINATION - RECYCLE.

The recausticizing plant in all the mills in this country operates with once-through use of purchased lime with the exception of a few rayon pulp mills having rotary kilns for reburning lime mud. This tail end operation of the soda recovery section functions as an open loop and the lime mud is discarded as a solid waste. This loop can be closed by a suitable calcination system and would offer significant cost savings and operating benefits. The use of reburned lime would improve causticization efficiency and give better settling characteristics during white liquor clarification. Accelerated rates of processing in the causticization section can also entail a substantial increase in

the causticization section can also entail a substantial increase in through-put besides ensuring a uniform concentration of active alkali in the white liquor for pulping.

With the changing trends in raw material mix towards increased hardwood utilisation, the silica content of lime mud will reduce and would become amenable for satisfactory calcination. A desilication step can be included for the removal of silica from black liquor, where necessary. Satisfactory operation of the calciner can be maintained by keeping the silica levels below the tolerance limit. Lime sludge can be reburned either in conventional rotary kilns or a fluidized bed calciner can be maintained by keeping the silica levels below the tolerance limit. Lime sludge can be reburned either in conventional rotary kilns or a fluidized bed calciner using fuel oil. The thermal aspects of reburning lime mud in a fluidised bed calcination system were high-lighted in one of the earlier IPPTA conferences by the author (4). Thus, a major solid waste disposal problem at many mill locations can be resolved and the causticization plant operated in a closed loop during pulping chemical recovery.

6. SUMMARY

The major sources of liquid and solid waste generation in a paper mill are identified and technological developments in pulping chemicals/energy recovery and wastewater treatment for upgradation and reuse are high-lighted and the implications of an efficient lime mud reburning system emphasized in this presentation.

REFERENCES:

1. A.G,Kulkarni; R.M. Mathur and R.Pant 'Ferrite Process - An Alternate Chemical Recovery System for Small Mills', IPPTA Annual Conference, March 17,18, 1983, New Delhi.
2. K.N.Maddern 'Mill Scale Development of the DARS Direct causticization Process', Pulp and Paper Canada, 87(10):1395 (1986)
3. R.D.Mittal and H.Veeramani 'Biogas Generation from Bagasse Black Liquor by Anitron system', IPPTA Zonal Meeting, December 11-12, 1986, Bangalore.

4. H.Veeramani and P.S.Prabhu 'Thermal Aspects of Lime Mud Reburning , IPPTA Annual Conference, March 18-19, 1985, New Delhi.