Chemical Recovery Systems in Mini Paper Mills

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ABSTRACT

The paper describes the different chemical recovery systems suitable for mini paper mills based on Agricultural residues. Utilization of by-products of spent liquors and various uses of lignin isolated from black liquors have been dealt with. Suitability of chemical recovery systems and their advantages and limitations are also discussed.

INTRODUCTION

In near future, a number of agricultural residue based small and medium size paper mills are likely to be installed in the country. The number of small paper mills have increased at an astonishing pace in the last few years. About 50 mills were started in 1979–81 alone and more are on the way. The present situation is not healthy for small paper mills because most of them have no proper chemical recovery systems. Mills without chemical recovery will be discharging valuable chemicals worth crores of rupee[5] and at the same time will cause considerable amout of pollution problems. Direct disposal of spent liquors not only creates a grave problem of polluting ground water but also is wasteful. Conventional treatment methods are capable of removing upto 90–95 per cent BOD. Other pollutants such as particulate matter, COD, sludges, acidity, alklianity can also be removed by appropriate methods. Paper mills having capacity upto 50 tons per day can not afford and find it difficult economically to recover, renovate and reuse spent liquors using conventional recovery systems. It has been reported that a 30 tpd mill is discharging sodium hydroxide worth Rs. 2.5 crores annually. The recycling of spent liquor will provide a solution for effective reuse of residual caustic in spent liquor and reduction in pollution load. The capital costs of conventional recovery system are very high and would range between Rs. 1.5-2 crores. Considering huge capital cost of conventional recovery system, a need for alternative process for recovery of chemicals is badly felt. In India almost all small mills based on agricultural residues, are using soda pulping. Proper approach is required to convert lignin-cellulosic solids waste to useful organic chemicals or to separate organic chemicals values in form of lignin preponalious from spent liquors and then treat the effluents with available methods to reduce BOD, COD, colour, alkalinity, acidity etc.

By–Products from spent pulping liquors

Pulp and Paper industry has a very huge lignin potential. If the means could be found to isolate it from spent pulping liquor and to convert it to usable chemicals, the financial returns might be sufficient to support separation and processing lignin preparations from spent liquor, thus helping stopping of stream pollution.

Alkali lignin could be isolated from soda process black liquor by neutralizing it with CO_2 from stack gases to pH 8.3 to 8.5. Almost 40% of the lignin could be further precipitated by addition of sulfuric/hydrochloric acid. The precipitated lignin could be changed to a crystalline, easily filterable and quick setlling form by using of water-imisiable solvent such as chloroform, methylene bromide etc. with lignin containing liquid such as soda black liquor. The chloroform or other agent may then be recoverd from the filtered liquid by vacuum or steam distillation.

Lignin thus isolated could be converted to a large surface area lignins useful in drug formulations for

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absorbing acids in the digestive system. due to their extremely high surface area and their acid-alkali resistence. Other suggested uses include carriers for adhesives, catalyst substrate, reinforcement for plastics and carriers for insecticides and herbicides.

Lignin adducts with 3-chloro-2-hydroxy-propane-1-sulphonate, chloromethane sulphonate, acrolein and the like compounds are also reported to be useful as surfactants in dye stuff compositions.

An adhesive from kraft or soda black liquor was prepared by reacting the black liquor (dry matter more than 25%) with a formaldehyde and combing the product with separately prepared phenol formaldehyde adhesive.

Lignin preparations from pulping liquor chemically modified by reaction with compound such as formaldehyde, triazines, alkyl amines were proven to be useful as coagulants, intreatment of sewage and other wastes. Cataionic water soluble lignin amines were useful for a variety of uses such as flocculating agents, coagulants, retention aids, dispersing agents, asphalt emulsifiers and emulsion stabilizers. Chlorobrominated lignins were highly effective fire retarding agents.

Utilization of spent liquor much depends on economic separation of its organic chemicals values and inorgonic chemical values from it. Modern techniques using Reverse Osmosis (RO), Ultrafiltration (UF), Electrodialysis (ED) have opened new horizons for treatment of spent pulping liquors particularly from small paper mills economically.

Chemical Recovery Process

Following methods are the alternative developed and commercially tested for processing black liquor from small paper mills based on agrowastes.

1) Wet air oxidation process and

2) Ferrite process

Wet air oxidation process

The basic principle of the process is oxidation of organic constituents of black liquor by air under high pressure and temperature to give a green liquor. The weak liquor is directly converted to green liquor eliminating the conventional evaporation and combustion steps. This method appears to be satisfactory for handling the viscous and high silica content black liquor.

Ferrite Process

Recently efforts were made on recovery of sodium hydroxide by autocausticizing methods using amphoteric oxides. The ferrite method using Fe_2O_3, was found to be a promising one.

This process was invented and patented by Toyo Pulp Company of Japan. This process is mainly applicable to nonsulphur black liquor to recover sodium hydroxide. In this process the spent liquor is burnt with ferric oxide at temperature of 850 °C. Combustion product when hydrolysed gives sodium hydroxide and ferric oxide. This process is promising and suitable for use in small paper mills due to its simplicity and lower capital investment.

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 agricultural wastes (Capacity – 30 TPD) using 10% active alkali (as NaOH) with pulp yield of approximately 45% will discharge spent liquor as caustic equivalent to about 1800 tons per annum. Potential energy loss represented by calorific value of black liquor solids can be shown be equivalent to about 6500 tonnes 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 expenses besides accounting for 75–80 per cent of the total pollution load (BOD) released by the mill as waste requiring treatment.

Before considering several viable methods for chemical recovery in small paper mills, some of the issues pending to be resolved relevant to mini operations are given below.

a) Optimum size of the mill for an ecomomical recovery system.

b) Improvements in pulp mill operations

c) Adverse effects of silica in black liquor during processing

d) Low energy potential of black liquor solids and needs for auxiliary fuel during combustion

e) Need for compact, low cost system

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

SUMMERY

The mini paper mills based on agricultural residues do not have chemical recovery system due to their financial constraints. It is possible to introduce recovery system and utilise the By–products of spent pulping liquor based on methods discussed in the paper. Black liquor can be conveiently processed employing the wet air oxidation process and ferrite process. However before adopting any of the process it is utmost important that the mill should be economically viable.

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