A Critical Review of Chemical Recovery Systems Available For Agro Based Paper Mills

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ABSTRACT

Expansion of paper industry since the early 70's has been in the small and medium scale sectors with capacities ranging from 10 tons to 50 tons per day. Most of these units use agricuitural residues as a major raw material adopting soda pulping process. Because of the proliferation of these units and non-availability of a viable recovery unit, these mills are causing heavy pollution load, making it nocessary for Technologists to look for a suitable solution to this ever aggravating problem.

There are many technically feasible recovery systems available at the international level, but we as Technologists with the active participalion of financing bodies have to find a financially viable system for such small units.

It is suggested that the Wet Air Oxidation system or the Wet Cracking process be adopted in India with suitable modification to suit our needs.

However, till a viable system is commercially established, the recovery systems already available in India could be set up in bagasse or wheat straw based mills above 30 tons per day capacity. For smaller units, anaerobic digestion system to gene·ate methane gas, which is used as a fuel, could probably be an alternative to take care of the effluent load.

Introduction :

When Pulp and Paper industry in India was in the early stages of development at the beginning of this century, using sabai grass and bamboo. the capacities were in the range of 20 to 30 tons per day and the technology available for recovery of chemicals was very primitive and labour intensive with very poor recovery efficiencies and with little or no thermal recovery.

The first modernisation of recovery system came into existence in India in the1950's and 60's with the installation of rising film long tube vertical evaporators B & W—Tomlinson, J.M.W. and C E. type Recovery Boilers and continuous causticising plant. This system with multi stage counter current continuous vacuum drum washing system could raise the chemical recovery efficiency to 80—90 percent level with comparatively efficient thermal recovery. The units were of capacity equivalent to 60 tons to 200 tons per day of pulp. There have been many further developments in the world in chemical recovery system for the past two decades, which have taken into account the following aspects :

— elimination of malodorous gases.
— maximum chemical and thermal recovery efficiencies.
— trouble free and hazard free operation.

However, in our country, we have yet to catch up with these modern developments. Instead, another development in our pulp and paper industry has taken place during this period, namely, establishment of small sized paper mills in the capacity range of 10 to 50 tons per day, using agricultural residues as their major raw material.

Problems Peculiar to India :

Since early 70's, there has been a rapid growth in the installed capacity of paper and board mills in India with the establishment of medium and small sized paper mills using agricultural residues and waste paper. Table No. 1 indicates the break-up of the number of mills under the different capacity groups.

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TABLE No. 1

Categorywise Capacity Distribution in India—1986 (1)

S. No.	Category	No. of Units	Installed Capacity per annum
1.	Above 20,000 TPY.	29	1,357,000
2.	10,000—20,000 TPY.	18	278,000
3.	5,000—10,000 TPY.	75	623,000
4.	2,000—5,000 TPY.	93	312,000
5.	Less than 2,000 TPY.	56	85,000
		Total	2,655,000

With the proliferation of medium and small sized units on such a large scale, there have been many problems faced by these units, and the most important amongst them to be taken care of at the present juncture, is a technically feasible and economically viable chemical recovery system suitable for these units.

Amongst the small and medium sized units, there are non integrated units based on waste paper and purchased pulp which do not have this problem. It is only in the integrated small and medium sized units using the agricultural residues that the problem of chemical recovery has cropped up. The problem has agravated because of the high cost of the cooking chemicals and pressu e on reducing the stream pollution.

Table No. 2 gives the effluent load on agrobased small/medium sized integrated units without recovery as compared to large integrated units having recovery units.

TABLE No. 2

Characteristics of Effluents from Different Types of Indian Paper Mills (2)

S. No.	Particulars	Large integrated mills with recovery	Agro-residues based mills without recovery	Waste Paper based Mills
1.	Raw Materials	Bamboo hardwoods	Bagasse, Straw, Rags etc.	Waste Paper
2.	Volume of waste water M^3 /ton	250 to 350	200 to 380	70 to 150
3.	pH	6.0 to 9.0	6 to 8.5	6 to 8.5
4.	Suspended solids mg / l	300 to 450	400 to 1100	350 to 900
5.	B. O. D. 5 20°C mg / l	100 to 160	220 to 1100	100 to 270
6.	C. O. D. mg/l	500 to 700	2000to 4800	470 to 900
7.	Lignin mg/l	80 to 100	300 to 700	—
8.	Sodium mg/l	30% to 60%	200. to 550	—
	Pollution Load kg/ton :			
1.	Suspended Solids	100 to 150	90 to 240	50 to 80
2.	B. O. D.	35 to 50	85 to 270	10 to 40
3.	C. O. D.	150 to 200	500 to 1100	50 to 90

The table indicates enormity of the effluent load from agrobased integrated mills without recovery. It will be a difficult task for these mills to economically treat effluent in order to satisfy discharge standards set up by State and Central Government Agencies. It goes without saying that these units have to plan, sooner or later, setting up recovery plants. In the long run, recovery units would be more economical than going in for elaborate effluent treatment arrangement, which is not only un-productive, but also difficult to manage if discharge standards are to be maintained rigidly. Moreover, la ge lagoons storing effluent can be deleterious to environment as well as the sub—soil water source.

With the depletion of our forests and very little effort by industry and the government to establish large scale plantations of suitable species to feed the paper industry, our country has no other alternative but to depend upon agricultural resi lues for further development of our pulp and paper industry.

Characteristics of Black Liquor From Pulping of Agricultural Residues .

It is very well known that the black liquors from pulping of agricultural residues are different in physical and chemical properties from those of conventional raw materials. A major difference which is of consequence to Recovery operation is that the former ones have high silica content and exhibit high viscosity at higher concentration. Thereby they make the conventional recovery system unsuitable.

Trends in The Development of Chemical Recovery For Agro Based Pulping Process In India :

As already indicated, large sized mills are mostly based on bamboo and hardwoods using sulphate cooking process. There have been problems in the past in the operation of recovery plants in the conventional units due to the peculiarity of the black liquors from these raw materials as compared to those from softwoods used in developed countries. The Indian paper industry, with the active involvement of equipment designers and manufacturers. has been able to fully take care of these problems during the past two decades. However, our experience in handling agro based black liquor has been limited. There are comparatively, few such units working successfully in the world today and India is no exception.

The cooking process generally practised for agricultural residues is soda process, which is found quite suitable for our country. There have been several units set up in the country using bagasse, but hardly few of them have recovery units, with the exception of M/s. Tamilnadu Newsprint & Paper Mills, which has been a pioneer in running a modern recovery unit based on bagasse black liquor alongwith hardwood black liquor.

New Technologies For Processing Spent Liquor From Agro Based Pulping Plants :

For consideration of the technical aspect of the recovery operation for small paper mills, an attempt is made here to present some of the latest technologies available in the world for recovery of chemicals suitable for agricultural residues.

1. Wet Air Oxidation Process :

This process is applicable for soda pulping process and is based on the chemical reaction between weak black liquor and oxygen. An elevated temperature of around 300°C to 320°C is required to achieve good oxidation efficiency. The exothermic heat of reaction is removed by the aqueous phase which is partly converted to steam. Typical pressure for soda black liquor recovery system would be 175 to 200 kg/cm^2 in the reactor.

The oxidised liquor consisting of a concentrated solution of sodium carbonate is discharged from the process and can be processed further in the recausticising plant.

The recovered liquor is practically colourless. Dregs containing the majority of the inorganic impurities present in the fiber, including silica, settle out prior to recausticising and are removed. Conventional causti cising operation is followed. Lime sludge can also be reburned to recycle lime.

Energy recovery from the reactor exhaust vapour can be done in the form of steam and power.

The biggest advantage of this process is that it will be ideally suited for the soda pulping of rice straw or any other silica rich raw material, since no evaporation and smelting are required.

However, this system, though very efficient and the most appropriate for agricultural residues, has not made any inpact mainly because of its high capital cost.

It is found that the capital cost for a 30 tons per day pulping plant would work out to Rs. 3 to 4 crores which is prohibitively high for this capacity plant. M/s. Zimpro Inc., USA, who own the patent for this process, have recently entered into technical collaboration with M/s Larsen & Toubro Ltd. Bombay for design, manufacture and supply of this system. It is not yet known, whether any paper mills in India have come forward to establish this recovery system.

A full fledged system is in operation at Associated Pulp & Paper Mills Ltd., Tasmania,, Australia to process Soda pulping black liquor from Eucalyptus. They have also tried non-wood fibre black liquor successfully and are quite confident in using this system for any silica rich black liquors.

2. Copeland System[4] :

The Copeland sytem is being offered by M/s Copeland Systems Incorporated, U.S.A. This process is again suitable for only soda cooked black liquors.

The process involves combustion of the black liquor in a fluidised bed reactor for the purpose of recovering sodium carbonate and, simultaneous complete and pollution free destruction of the organic pulping residues. The liquor concentration for infection into the fluidized bed reactor is around 34—35 precent total solids. The recovered pelletized soda ash can be dissolved in water or weak wash and processed through recausticising system to get caustic soda recycling.

Since the concentration of black liquor require for firing into the reactor is only 34—35%, the problems of scaling in the evaporators due to silica is not so predominant.

A low temperature of around 650°C is maintained in the reactor, in order to keep the inorganics in solid, granular form. The inorganics in granular from are withdrawn through the side of the reactor through a variable speed screw conveyor and fed to the dissolving tank.

The bed material is kept in a fluidised state by the flow of combustion air.

For particulate recovery from the flue gases from the reactor, a dry cyclone is used in the first stage. The dust collected is discharged into the dissolver. The gases then pass through the incoming semi-concentrated black liquor from the evaporator is used in the venturi scrubber as a scrubbing medium.

A major advantage of this system is that the unit is safe from explosion hazards since no smelt is generated and that the boiler, which acts only as a waste heat boiler, is physically separated from the bed containing the chemicals.

This unit is in operation in some of the bagasse based pulp mills of Latin American countries. One such unit was established in Syria in the early 80's to process straw black lipuor.

Unfortunately, there is no authentic data available on the performance of this unit and its suitability to adopt for Indian small paper mills. Unofficial reports have indicated that there have been serious operational problem in some of these units, especially at the Syrain Mill because of the tendency of the ash to melt due to fluctuations in the Reactor temperature.

3. BKMI Process[5] :

This system of chemical recovery was designed and developed by M/s. Babcock Krauss-Maffei Industrieanlagen GmbH, (BKMI) West Germany. The system was specially designed for processing rice straw black liquor which is high in silica content. The first such system has been supplied and installed by BKMI for National Paper Corporation, Sri Lanka to process rice straw black liquor.

The system involves evaporation of black liquor upto 35–37% concentration as a first step. The last two effects of evaporator system where the black liquor has the highest concentration are of falling film type. The design takes care of the silica problem.

The evaporation from 35—37% total solids to about 50%solids is carried out in a direct contact evaporator of cyclone evaporator type. The liquor at 50% solids is pumped to the furnace by screw type pumps.

The concentrated black liquor is burnt in a rotary kiln. The kiln is so designed as to evaporate the black liquor and then convert it into soda ash before being discharged from the kiln. The temperature in the kiln is kept under control to avoid formation of smelt.

Since the smelt formation is totally avoided, the problem associated with silica in the black liquor is eliminated.

The flue gases from the kiln are led to waste heat boiler for recovery of heat.

The soda ash discharged from rotary kiln is dissolved in weak wash and then processed in the recausticising plant. In the recausticising section, the clarification of the causticised slurry and subsequent lime mud washing are done only on rotary belt filters and excepting green liquor clarifier no sedimentation type clarifier is used. This has been done to take care of the slow settling rates of silica rich lime sludge.

This unit was installed some time in the late 70's in Shri Lanka. However, there were many operational problems in the beginning which were attended to by M/s. BKMI. It is not known as to how it is working at present. This system again is capital intensive and since no data is available on its performance, it is difficult to come to any conclusion about its suitability to small mills.

4. Smelter Cyclone Evaporator Unit :

An attempt was made at M/s. Andhra Pradesh Paper Mills Ltd. in the early 70's to design and develop a unit suitable for agro based, silica rich black liquors. The unit is generally known as 'Gopi Smelter' and four such units were in operation at Andhra Pradesh Mills Ltd., as well as West Coast Paper Mills, till a couple of years ago. The system involves evaporation of weak black liquor upto a concentration of 18-20 % in multiple effect evaporators and further concentration upto 50% solids in a cyclone evaporator. The concentrated liquor is fired into refractory lined furnace. The furnace is similar to conventional smelter but there are no water cooled walls excepting the roof.

Hot flue gases from the furnace as they come out of the chamber are cooled by flue gases recirculated from the cyclone evaporator outlet. The gases thus cooled are at 350°C which are led to the cyclone evaporator. The cyclone evaporator is so designed as to concentrate the incoming black liquor of 18-20% solids to the final firing concentration for 50% solids. The outlet from the cyclone evaporator has a temperature of 150°C which is partly recirculated as mentioned above.

The secondary recovery for particulate emission can be done in a venturi scrubber where the incoming black liquor from the evaporator is used as scrubbing medium.

Though, the unit is versatile with a low capital investment, it suffers from one drawback under the present situation created by the high energy costs, namely, that there is no steam generation from this unit. Attempts have been made to incorporate a waste heat boiler before the cyclone evaporator but its performance is yet to be observed. The recovery efficiency can be close to a conventional recovery unit provided the secondary recovery system is incorporated.

5. Destromax Recovery System :

This system is being offered by M/s. Thermax Private Limited, Pune. This is similar to the item No 4 mentioned above excepting that a Boiler is incorporated after the smelter.

The weak black liquor has to be evaporated to 35-40 percent solids in the multiple effect evaporator and further to 50-55 percent in cyclone evaporator before firing into the smelter. The refractory walls of the smelter conserves the heat in the furnace at a higer temperature and this enables firing of black liquor from agricultural residues without the help of any auxiliary fuel.

A venturi scrubber recovers the particulates from the flue gases. Weak wash from recausticising plant is used as a scrubbing medium before supplying it to the smelt dissolver.

One such unit is under installation in a bagasse based mill in Andhra Pradesh.

6. Recovery System Developed In China :

In the People's Republic of China, just as in India, the basic raw material for paper making is straw and other non-wood fibres It has more than half the number of world's mills but mostly of small capacities. About 60% of the fibres used for paper making is from nonwood plants, mainly wheat and rice straw. Though, an attempt has been made to plant fast growing tree species, straw still dominates as the major raw material.

Just as in India, China has a high proportion of small paper mills which cannot afford sophisticated chemical recovery and other pollution control systems and hence there has been R & D efforts to find out a new process for pulping of straw.

Use of neutral ammonium sulphite for pulping which produces spent liquor that can be used as fertiliser has been successfully tried[6].

In another R&D effort[7] carried out by Mr. Tan Long of department of Chemical Engineering, Tianjin Institute of Light Industry, Tianjin, People's Republic of China, wet cracking of rice straw black liquor has been tried. As the result of the initial trials, a prototype unit of capacity equivalent to 5,000 tons per annum of straw pulp has been established last year. The performance of this unit are not known.

In wet cracking, black liquor is reacted at high pressure and high temperature in the absence of oxygen or any additives. During the process, carbohydrates are cooked, dehydrated, and taken out as a char powder. Lignin and other organic matter get converted into wet cracked gases which consist of the methane, ethane, hydrogen, and carbon dioxide, and tar oil. The sodium silicate contained in the original black liquor is converted in to silica (silicon dioxide) which comes out alongwith the char powder as an insoluble mass. Alkali is dissolved in water or weak wash. The insolubles are removed from the system by any of the conventioned separation systems and the Sodium Carbonate obtained is recausticised in a conventional system.

In this system it is claimed, up to 95% of the organic matter present and 96 to 99% of silica are removed from the system. The wet cracked gas can be used as a fuel for generation of steam. The sludge from the recausticising plant contains very little amount of silica and hence can be recycled.

The weak black liquor from the washing system needs to be evaporated only upto 16% solids before wet cracking and hence the problem of evaporation is also reduced.

It is claimed that the investment in this type of unit is less than half of the total cost of a conventional chemical recovery plant, and recovery efficiencies of 85 to 90 % are achievable.

7. Straw Pulping in European Countries[8] :

Hungary has been a major consumer of straw, mainly the wheat straw for production of paper. The chemical recovery system generally used is a conventional recovery system having evaporators, recovery boiler and recausticising system. It appears that they are working satisfactorily, but the capacities are generally high.

In greece, at Thessalin Pulp and Paper Mills where wheat straw is the major raw material, a conventional chemical recovery unit has been in operation since more than a decade. But the capacity is over 100 TPD of straw pulp.

8. Development of Recovery System at Rakta Paper Mill, Egypt[9] :

It has been reported that one of the world's biggest rice straw based mill operating in Egypt without recovery has achieved encouraging results in developing a system for removal of silica from the black liquor to make it suitable for processing in a conventional recovery system. The work was carried out in collaboration with Lurgi of F.R.G. The process is still in the pilot plant stage and a commercial scale operation of a capacity 200 tons per day of pulp production is likely to be started in 1988.

9. R&D Efforts In India :

(a) UNIDO Sponsored Research Project :

Under the above R&D programme, Pilot plant trials have been undertaken at the Central Pulp Mills Ltd., Fort Songadh, Gujarat in collaboration with CPPRI, Dehra Dun to disilicate the bamboo black liquor. This work was carried out between 1983 to 1985 under the guidance of UNIDO experts. On the basis of research work, a full fledged production unit has been designed and the plant is being set up at the Kerala Newsprint Mills.

In this system, weak black liquor is treated with the flue gases from the recovery boiler to bring down the pH to the silica precipitation level and after removable of the insoluable silica sludge, desilicated black liquor after raising its pH is sent to the evaporator section.

b) Many other R & D efforts are in progress at I.I.T., Bombay, CPPRI, Dehra Dun and many other R & D laboratories of many of the Indian Pulp and Paper Mills. However, it is difficult to say at present as to when all these efforts would be converted into commercial scale operations.

10. Other Alternative System Suitable For Small Paper Mills :

It has been discussed on and of that for agro based pulping units less than 30 tons per day capacity, a chemical recovery plant is not economical because of the high capital cost and low heat and chemical recovery efficiencies. The only alternative could be to treat the black liquor in an anaerobic digestion system. One advantage of this system is that it can generate methane gas which can be used as a fuel for steam generation. However, chemical recovery will not be possible. It is claimed that the fuel saving upto 30-35% can be achieved in this system by burning the methane gas. A few small paper mills have come forward to set up this unit with foreign collaboration and the results are still awaited.

Conclusion :

With the technologies and equipment available in India, it will be difficult to recommend any chemical recovery system for agrobased units of less than 30 tons per day capacity because of the high capital cost involved. Units larger than 30 tons per day based on bagasse, wheat straw and other raw materials not so rich in silica, should go in for the recovery systems available and well established in our country though the initial investment will be high. For rice straw based mills, there is no technically feasible system available, since all the R & D efforts in this direction are yet to be established on a commercial scale.

However, the economics for the abovementioned systems have to be worked out on individual basis and depend to a great extent on the location and cost of various inputs in each case. Hence it is difficult to generalise the economic viability. Hence no attempt is made here to project any financial workings on the recovery operation.

For units below 30 tons per day capacity, the Anaerobic digestion system with the generation of methane gas could probably be an alternative to take care of the effluent load.

There have been many R & D efforts and technological breakthroughs all over the world including India, to find a suitable chemical recovery system for nonconventional raw materials. But it is unfortunate that we in India are yet to come out with a suitable system for our small Paper mills. R & D efforts presumably have to continue till a technically feasible system is established and commercially exploited, keeping in view the capital cost and the running cost, which these mills have to absorb.

In the opinion the author, the Wet Air Oxidation system developed in U.S.A. and the Wet Cracking Process being developed in People's Republic of China have tremendous potential for adoption in India provided they are suitably modified or simplified to suit our agrobased small and medium sized paper mills. It is suggested that the Central Pulp and Paper Research Institute, Dehra Dun and other Research Institutes and R & D Departments in Paper Industry continue their efforts in this direction till a commercially viable solution is found out.

It is also suggested that the Financial Institutions come forward to provide Venture Capital to finance such R & D efforts and to transform such efforts into commercial production.

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