Chemical Recovery Options For Agro Based Pulp And Paper Mills

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ABSTRACT:-- The agrobased paper mills have open to them a number of options for selecting an appropriate chemical recovery system depending upon their black liquor properties and size of the mill. Since this is a capital intensive area which needs technical expertise and good control, sufficient feed back on the various process technologies is essential. Armed with the complete information on their black liquor characteristics and accordingly selecting a recovery process will go along way in enabling the mill to achieve the maximum chemical recovery efficiency with minimum of down time. The paper discusses various chemical recovery technologies available to agrobased mills and their operating experience.

INTRODUCTION

A number of agrobased paper mills have enhanced their production capacities from 20-30 tpd to almost 100 tpd level and are no more classified as small mills. As a result they can no longer afford to dispose off their effluents specially the black liquor and other pulp mill waste water, due to environmental and economic reasons. This has led to a frantic search for a suitable chemical recovery process, which would be capable of handling low solids and high fouling liquors difficult to burn. There are now several options available to the agro-based paper mills, and some of the mills have already gone ahead with installing Chemical Recovery system.

The efforts to find a viable solution to chemical recovery for agro-based sector began with a sizable output by CPPRI in terms of useful information gained regarding physico chemical properties of black liquors which were poorly understood. Today with the systematic analytical data available on rheological and thermal behaviour of agro residue black liquors, the boiler designers are able to make necessary changes to take care of black liquor combustion. Significant work has also been done at the Institute on pulp washing, evaporation, viscosity control and desilication of agro residue black liquors. Some of the case studies on recovery installations and other emerging technologies are discussed below:-

DISCUSSIONS

CHEMICAL RECOVERY INSTALLATION AT SATPUDA PAPER MILLS

Supplied by Tunghbhadra machine and Tools (TMT), the chemical recovery system at Satpuda Paper Mills has a designed capacity of processing 65 tpd dry black liquor solids based on soda bagasse process. The plant is provided with five effect LTV evaporators followed by Forced Circulation Evaporators to achieve a concentration of 45%. The steam economy is about 4.2. From the evaporators the thick black liquor is sent to cyclone evaporator located in the flue gas stream of recovery boiler and the concentration is increased to 55%. A venturi

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scrubber is provided for the secondary recovery. One ID fan is provided after the cyclone evaporator and another ID fan after the venturi scrubber. The smelt formed is dissolved and is sent to causticizers to produce 13 tonne per day of caustic at 100 g/l T.A.A. as NaOH. The causticity achieved is 80%.

Operational Experience

Experience with Evaporators

- The five effect evaporators are operated without any standby body.
- In view of high viscosity of soda liquors, forced circulation evaporators were provided to raise the concentration upto 45% but keeping RAA at 8 g/l the problem of viscosity was overcome and desired concentration is achieved in MEE.

Experience with Recovery Boiler

- Autogenous combustion is accomplished and no oil support is needed during the operation of the system.
- By adopting three tier air system and proper preheating of the air, blackening and smelting problems are overcome.
- No chemical carry over and no hard deposits of chemicals are experienced and hence no soot blowing is required.
- No problems are experienced during regular restarting. Oil consumption during cold start up is very low and is in the region of 1.5 KL.
- The furnace is flexible and allows the unit to operate at low loads as well as high loads without problem. The trials at 120% rating were found to be smooth and satisfactory.
- The boiler operation is very simple and can be operated by local hands with short training course. The recovery efficiency is about 86%.

Status

The plant is running smoothly and continuous since its commissioning in October'93. No shut down has taken place during its 29 months of operation. It is a viable option for existing mills that are using bagasse as a raw material and are planning expansion. Also the units that are operating on waste paper and considering to switch over to bagasse pulp can go for similar chemical recovery system without any reservations.

Brief Operating Results are as Follows:-

	Evaporator		Recovery Boiler		Causticizer	Total
	LP	MP	LP	MP	LP	
Steam Required t/h	5.14	0.70	0.30	1.95	0.65	8.84
Steam Generated t/h	--	--	--	7.50	--	7.50
Net Steam Required t/h	--	--	--	--	--	1.24
Power Required KWh		52	320		100	472
Oil Required KL/day		--	0.4		--	0.4
Lime t/day		--	--		18	18

Based on the above operational results the direct cost of the recovered caustic is generally as follows (with BSW losses assumed at 18 Kgs/T of pulp expressed as Na_2SO_4 and liquor sent to evaporators is at 9% concentration).

		Cost/day (Rs.)	Cost/Tons of caustic (Rs.)
Net Steam cost	29.72 X 400 =	11904	916
Power Cost	11328 X 2.6 =	24453	2678
Oil Cost	0.4 X 6000 =	2400	185
Lime Cost	18 X 1200 =	21600	1266
		63869	5045

RECOVERY INSTALLATION AT SHREE VINDHYA PAPER MILLS

The mill is using bagasse as raw material and have undergone capacity expansion to the present capacity of 100 TPD. The mill is having dry depithing system. The chemical recovery system involves concentration of weak blak liquor (9-10%) to a level of 45% in Multiple Effect Evaporator followed by Cascade Evaporator to increase the concentration upto 60% before firing. In the recovery boiler the combustion air is supplied at 3 levels. Primary and secondary nozzles are located below the black Liquor spray and tertiary air nozzle above the spray zones. Primary and secondary air are proportioned in such a way that the combustion is completed in the lower furnace zone and the tertiary level air nozzles are provided to burn any left over particles so as to contain the carryover of burning black liquor particles.

The boiler is of single drum with a flexibility of locating the steam drum outside the flue gas path. The spout for tapping the molten mass is positioned at rear wall of the boiler i.e. under the nose to

prevent smelt blockages.

Operating Experience

During the first three months, lot of problems were faced in handling the liquor due to high viscosity of the liquor which was later controlled by increasing the RAA in the liquor. Due to poor swelling, the burning characteristics were not satisfactory. Oil support was needed for about a month. After increasing the chemical charge to the digester and rationalising the cooking parameters, a remarkable change was observed in black liquor characteristics and boiler operation became smooth. Oil support was removed and the boiler started running even at 70% MCR load without oil.

Status

After the plant was commissioned by M/s Enmas Technologies at Shree Vindhya Paper Mills, during the first few months problems were encountered due to poor black liquor characteristics. With some changes in the process conditions, the boiler operation was stabilised in November'94, and since then it is meeting the requirement of the mill production. Apart from the recovery of cooking chemicals, the boiler is producing about 10-12 tons of steam at 42 Kg/cm^2 pressure and 400^{0}C temperature thus contributing to the captive power generation of the mill.

C) COPELAND SODA RECOVERY SYSTEM AT SHREYANS PAPER MILLS LTD.

In this process the semi concentrated liquor of 25-30% total solids from multiple effect evaporator (MEE) is fed to venturi scrubber of the Fluid Bed Reactor where hot flue gas reactor at 450^{0}C exchanges heat by direct contact black liquor is concentrated to 38% T. S for feeding to reactor. Steam is used to atomise the liquor. The hot flue gases in the reactor free board, heat the liquor spray and dries up to char solids. Fluidised bed condition is maintained by forcing fluidising air from an orifice plate underneath. The char solids burn to pellets of sodium carbonate and is discharged continuously from the reactor using variable speed metering screw. KIMBERLAY CLARK, Mexico had installed Copeland System in 1976 and was operating successfully since then. The unit was found bearing the original Copeland design and operating smoothly using 100% bagasse (Fig.1). KCM reported there was no chloride problem in

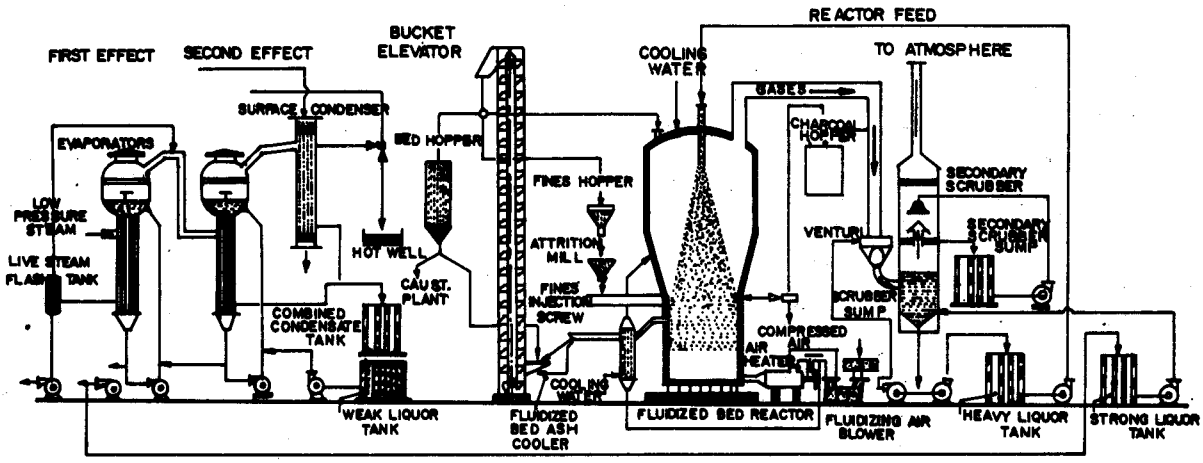

FIG. I, SCHEMATIC OF FLUIDIZED BED SODA RECOVERY SYSTEM AS PROPOSED BY AGRO PULPING MACHINERY (P) LTD.

their liquor and operation. The operating data of FB reactor at KCM are as follows:-

Bed Depth	50"
Bed Temp.	710°C
Free Board Temp.	450°
Fluidising airpress	0.4 Kg/Cm²
Fluidising air flow	30000 M³/min
Chlorides in B.L.	< 0.5%
Chemical Recovery Efficiency	95%
Steam Economy	3.2
Refractory Maintenance	10 Yrs
Cleaning Cycle	
- FB Reactor	6 months
- Evaporator	4-6 weeks

Operating Experiences

The giant mills of south Africa and Mexico like SAPPI, MONDE and KIMBERLAY CLARK have installed the Copeland Technology as early as 1972-73 and have been continuously operating without undergoing any change. Though, the presence of higher chlorides is always a negative factor for any combustion technology and hence also for Copeland Technology, the technology is equally applicable to softwood hardwood or bagasse. Equally the technology is widely applicable with pulp in processes like soda, sulphite, kraft etc., however, it may be noted that in case of sulphite or kraft, products are oxidised and is not in the form of direct reuse of pulping chemicals. Being a low cost investment, the FBR system is specially suited for the economics of small and medium range pulp and paper mills in India.

Status

Shreyans Papers, has installed fluidised bed reactor for soda recovery using bagasse, rice straw, wheat straw, sabai grass and jute waste as raw material. The technology has been supplied by Agro Pulping Machinery (P) Limited, Madras in collaboration with Enders Process Equipment Corporation, USA. The long and successful experience of South African Mill establish the fact that the Copeland Technology is a proven and competitive process for handling black liquor using various pulping processes and raw materials.

EMERGING TECHNOLOGIES

Among the various emerging technologies the following three technologies are identified as a viable options for agro paper mills.

- DARS/Ferrite Process
- ABC Recovery Process
- MTCI Indirect Gasification Process

DARS/FERRITE PROCESS

DARS i.e. Direct Alkali Recovery System is one of the outstanding development in the area of Chemical Recovery. The basic principle of the process involves combustion of concentrated black liquor and Fe_2O_3 or amphoteric oxides to obtain a solid product i.e. NaOH and Fe_2O_3 or other. The reactions are as below:-

Combustion

Black Liquor + Fe_2O_3 ----------> $Na_2Fe_2O_4$ (Na_2O)

Leaching

$Na_2Fe_2O_4 + H_2O$ ----------> $2NaOH + Fe_2O_3$ + Heat

In this process combustion and causticisation is accomplished in a single stage and single reaction vessel and is ideally suited for soda process. One major advantage is the absence of smelt in the system. The process is safe simple and flexible and also less capital intensive compared to conventional system.

ENERGY REQUIREMENTS FOR DARS RELATIVE TO KRAFT RECOVERY (1 tpd Basis)

	KRAFT	DARS
Digester Steam, GJ	3.47	3.40
Evaporator Steam, GJ	4.36	3.35
Fuel for Lime Kiln, GJ	1.71	0.00
Relative Change from Conventional, GJ	0.00	-2.79

RELATIVE ENERGY EFFICIENCY (1 tpd Basis)

Heat Input, GJ	23.15	23.08
Heat Losses, GJ	7.55	8.93
Heat to Steam, GJ	15.60	14.15
Thermal Efficiency, %	67.4	61.3

Operating Experience

A prototype pilot DARS plant is operating in CPPRI and the results obtained have been very

encouraging. White liquor concentration of 175 g/l and causticity upto 90% has been achieved. The plant operates on batch scale and needs continualisation for prolonged studies. The dust formation is slightly on the higher side and can be minimised by proper selection of ore and particle size. Autogenous combustion can be achieved at 48-50% concentration of the liquor. Efforts are being made to add required components to continualise the existing DARS plant at CPPRI, and to run it at an appropriate mill site.

ABC RECOVERY PROCESS

In this process, the semi concentrated black liquor (30-35% solids) is mixed with a solid fuel (organic waste such as rice husk) and fed to the furnace with a movable grate for incineration. Temperature is controlled to avoid smelt formation. The charred material is leached with water and filtered to reject carbon particles. The solution contains mainly sodium carbonate and sodium silicate. The green liquor is carbonated to remove silica which is separated by filteration. The clarified green liquor is caustisized by lime to generate white liquor. The white liquor concentration obtained is very low.

Status

Developed by M/s Amrit Banaspati Co. (unit paper), the technology is totally indigenous and needs considerable developments for commercialisation. The mill has however informed that they have decided to put up a mill scale plant at their site and the plant will be commercialised in near future.

INDIRECT GASIFICATION OF BLACK LIQUOR (MTCI PROCESS)

Manufacturing and Technology Conversion International (MTCI) Inc. USA have developed a process of Indirect Gasification of black liquor to produce a high calorific fuel gas (2000-2500 Kcal/ m^3). The gasification takes place in a so called "Thermo Chemical Conversion Reactor (TCCR). It comprises of a steam fluidised bed containing heat transfer tubes where black liquor is fluidised into

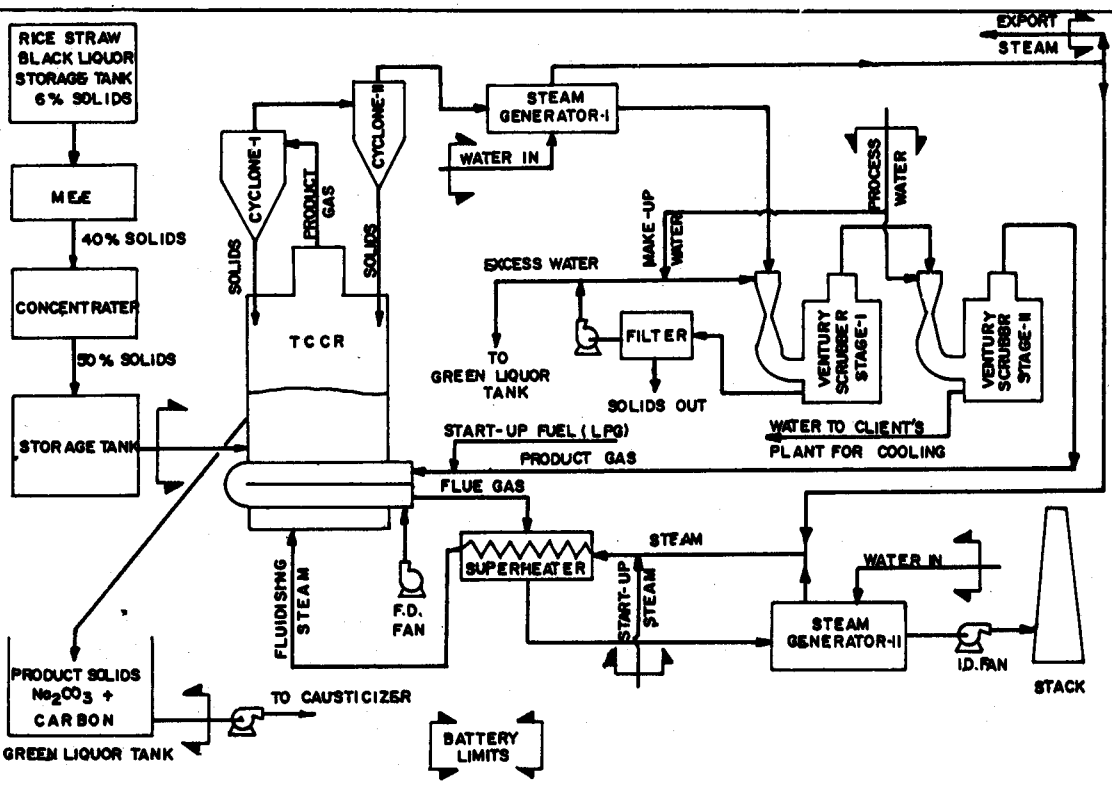

FIG. 2, SCHEMATIC OF RICE STRAW B.L. INDIRECT GASIFICATION SYSTEM AS PROPOSED BY ESVIN ADVANCED TECHNOLOGIES LTD.

the reactor black liquor solids undergo vaporisation and pyrolysis reaction. Higher hydrocarbons of the pyrolysis products are steam cracked and partically reformed to produce low molecular weight products. Residual char retained with in the bed is more slowly gasified by steam to produce fuel gas with high hydrogen content. The product composition is:-

50–60%	H_2
5–10%	CO
20–30%	CO_2
2–10%	CH_4

The gas produced can be refired into the pulse combustor which supplies the requisite heat for the gasification process. The pyrolysis takes place at lower temperature (530-630°C) to avoid melting of sodium salts. The sodium carbonate char is taken out of the reactor dissolved and causticized in a conventional way. In MTCI process pulse combustion heaters are used for indirect heating of the fluidised bed reactor. This gasification called Thermo Chemical Conversion Reactor (TCCR) combines three advanced technologies into one (Fig.2)

Status

A demopilot plant has been installed at Seshasayee Paper and Boards (SPB) having a capacity to process 500 Kgs of BLS/ hr. The process was demonstrated in a field scale test at the mill site of SPB, Erode with rice straw liquor. The demonstration proved that:-

- It is possible to gasify the liquor even at 40% solids.
- Silica present in the liquor remains as free silica in the bed.
- The gas composition was found to have calorific value in the range of 250 Btu/c ft and hence could be easily refired into pulse combustor.

So far, no commercial installation based on this technology has come up in India in a paper mill, but a sugar mill has adopted this technology to ignite the mills liquid waste.

ROLE OF CPPRI IN THE AREA OF CHEMICAL RECOVERY

Over the last 15 years CPPRI has been engaged in black liquor research and special attention has been paid to black liquor generated in pulping of agro waste raw material. Exhaustive analysis of agro-based black liquor including physico-chemical, chemical and thermal properties have been helpful in better understanding of these liquors and has been instrumental in modifying the conventional recovery process and developing alternate recovery process for agro based mills. Extensive basic research has led to the development of technologies like **"Desilication process for Bamboo Black Liquor and Thermal Treatment for viscosity reduction in bagasse black liquor"**.

With the development of these technologies the processing of black liquor has become easier which otherwise posed lot of problems in chemical recovery operation. Institute has also rendered assistance to the companies which have gone for commercial installations at Shreyans Paper Mills, Shree Vindhya Paper Mills and Satpuda Paper Mills.

The concept of modified Conventional Chemical Recovery is also being pursued by CPPRI looking into the time taken for developing new process technologies. In this scheme, institute proposes the following steps:-

- Vapour phase pulping of raw material under optimum cooking conditions to generate liquor with higher solids concentration.
- Washing of pulp using Horizontal Double wire washer to keep high solids in washing.
- Use of microsieves to filter black liquor.
- Desilication of Black Liquor having silica levels higher than 2 gpl by CPPRI carbonation process to remove more than 80% of silica.
- Use of falling film type of evaporator for increasing black liquor solids. If the option is not economical than at least last two effects where solids concentration is higher can be of falling film type.
- Liquor heat treatment using the process developed by CPPRI for reducing the viscosity.
- Use of modified recovery boilers with improved design to handle, low calorific value and low solids concentration of the black liquor.
- In the long term, to install lime sludge reburning for total system closure and reduced solid waste.

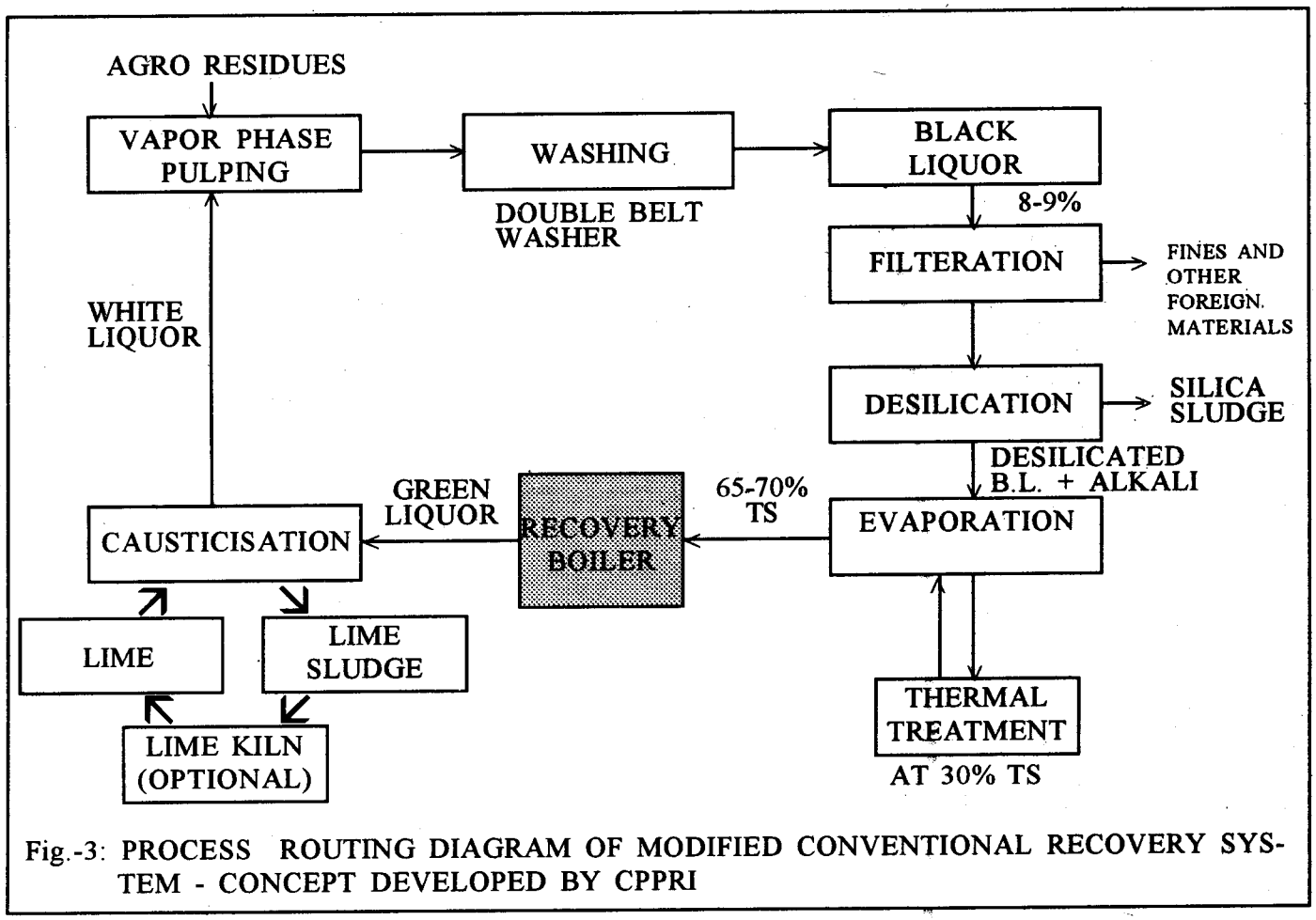

Fig.-3: PROCESS ROUTING DIAGRAM OF MODIFIED CONVENTIONAL RECOVERY SYSTEM - CONCEPT DEVELOPED BY CPPRI

Such a proposal was prepared for an agro based paper mill and submitted to the Ministry of Environment and Forests, New Delhi, which was accepted by the Government to grant assistance. It is in likely to be implemented soon. A process routing diagram is annexed (Fig.3).

Now, that a number of viable options are available to the agro based paper sector to select a suitable Chemical Recovery System. and there are already three such installation in agro sector, other mills should not wait any longer in making a decision to install a Chemical Recovery System depending upon the size of the mill and the raw material used. Chemical recovery for bagasse based mills has already been well established and practiced and with the inclusion of desilication and liquor thermal treatment other high silica and high fouling liquors from rice and wheat straw can be handled for the chemical recovery.

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