Soda recovery systems for small paper mill Issues and options

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ABSTRACT

The small paper mills play a significant role in filling the evergrowing gap between production and demand for paper and paper products. It is estimated that almost 50% of the demand is met by the production from small paper mills of capacity less than 30 tpd.

Although, these mills have an important role to play, none of them have a recovery plant thus leading to considerable loss of valuable chemicals and also causing serious environmental problems. The main reason for the malice lies in their small capacity and hence their inability to install any of the conventional Soda Recovery plants which are highly capital intensive. In addition the raw material being utilized by them in their production also complicates the issue.

This paper addresses some of the problem encountered by them and also reviews some of the recent technological innovations which probably could solve this complex problem

1. Introduction :

The demand for paper and paper products have been steadily increasing in our country since the last two decades. To bridge the gap in demand and supply. Government of India encouraged in the seventies, establishment of small paper mills based on non-conventional raw materials. All paper mills less than 10,000 tpd were grouped under the small mill category and received both concessions and fiscal incentives from the government and financial institutions. Most of the mills which came under this category were based on agricultural residues and recycled fibres and did not have any chemical recovery system.

Since then the number of small paper mills have proliferated many fold and currently produce nearly 50% of the total installed capacity of 3.0 million tonnes. The quantum of chemical pulp produced by these mills vary from a meager 5% to 100%. The

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balance raw material furnish consists of waste paper and imported pulp. Although it is heartening to note that these mills have considerably contributed to meet the demands, the lack of chemical recovery system forces them to discharge the entire black liquor into water streams/on land. It has been estimated that these mills discharge nearly three times the combined pollution loads of all big mills.

The principal reason for this malice is the non availability of suitable soda recovery system in their process. A direct consequence of this is the loss of more than 36,000 tpa of recoverable alkali and wastage of 90 million units of scarce power which could have been generated from the black liquor. In addition the growing awareness of the environmental problems

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encountered due to their discharge into receiving waters has attracted adverse publicity from the public and the Pollution control Boards. The pollution load from small paper mills using agrofibres as raw material is believed to be about three times in terms of COD and BOD and about four times in terms of lignin as compared to the big mills (with soda recovery systems.)

Table-1. Pollution loads from paper mills 1

Description	Big paper mills	Small paper mills	
Number of mills	30	275	
Installed capacity (m.tpa)	1.46 (48)	1 54 (52)	
Actual production (m.tpa)*	0.83	0.88	
Suspended solids (tpd)	298 (48)	328 (52)	
BOD (tpd)	+15 (25)	350 (75)	
COD (tpd)	493 (25)	1467 (75)	
Lignin (tpd)	65 (19)	275 (81)	

* Assumed to be 57% of the installed capacity. Figures in parentheses are percentage values.

Because of the growing problems of land availability and concerns raised on the possible increase in alkalinity of the soi!, the small paper mills are under greater pressure to fully treat their effluent. The MINAS limits nave to be achieved by all small paper mills sooner or otherwise they will have to face closure. Their expansion is also directly linked to incorporation of a suitable soda recovery system.

Besides pollution problems, the magnitude of caustic drained and the corresponding electrical power wasted can be appreciated from the following estlmates:²

1.	Total agro-based raw material consumed by small paper mills	4,00,000 tpa
2.	Caustic consumed at an average of 12% on raw material	48,000 tpa
3.	Recoverable caustic @ 75% recovery efficiency	36,000 tpa
4.	Electrical power required to generate this amount of caustic @ 2500 kWh/t	90 million units.

2 0. PROBLEMS ENCOUNTERED BY SMALL PAPER MILLS IN ADOPTING CONVENTIO-NAL CHEMICAL RECOVERY SYSTEM.

Most of the problems encountered by the small paper mills in incorporating an efficient soda recovery system can be summarized under the following categories.

Process technology deficiencies

- Limitations of size

- Raw material constraints.

2.1. Process Technology deficiencies.

Most of the small paper mills were conceptually designed for low capital cost and hence suffer from a number of inadequacies with respect to the process technology adopted. Some of the salient shortcomings are

- The raw material preparation in terms of efficient depithing of bagasse or wet cleaning of straw is not adequate.
- All the mills with very few exception use batch rotary/tumbling digesters and this results in low concentration of spent liquor due to high bath ratio maintained for cooking or due to one stage washing in digesters.

Many small mills have only two stage pulp washing and a few use only a single stage washing. Due to poor raw material preparation before pulping the washing efficiency is low inspite of using large amounts of washing water, leading to further dilution of the spent liquor. Thus they have very low concentrations. It is worth mentioning, at this juncture the importance of good brown stock washing in the efficient functioning of any recovery system.

2 2 Limitations of size :

Although most of the small paper mills are operating at capacity levels of 20.000 tpa, the chemical pulp, produced from agrifibres accedes 10 000 tpa in only a few mills. A recent survey¹ of the capacity production of virgin pulps revealed that only 30 mills are producing in excess of 30 tpd It has been well documented by a number of authors³,⁴ that the conventional Roaster/Smelter type of soda recovery system "is not viable or is only marginally viable even for chemical pulp capacity of 30 tpd. The main reason for this is the energy cost (Steam+Power) constitutes more than 80% of the total operating costs (excluding interest and depreciation). The more modern recovery systems are also not viable due to high capital cost needed for their installation. This means that the classical approach being adopted for the bigger mills is not viable for the small paper mills due to the high energy losses (in terms of fuel value in organics and electrical power in caustic) in the effluents discharged by these mills.

2.3 Raw material constraints :

The main raw material used by the small paper mills are bagasse and straw. While limitations of size are applicable to mills using either of the raw materials handling of straw possess yet other obstacles. In case of straw the problems of viscosity and silica add new dimensions to the problem of recovery. The desilication of rice straw black liquor has not been possible and even some of the recent processes demonstrated may not be economically viable for mills of even 30 tpd capacity. The rice straw liquors have higher viscosity and are colloidally unstable at concentrations above 30%⁵ and therefore conventional evaporation and combustion of the spent liquor are beset with problems that too difficult for small paper mills to cope with.

3 REVIEW OF SOME OF THE EMERGING TECHNOLOGIES.

The principal, factors which will ultimately de ermine the suitability and viability of any new process proposed are

1. Capital costs involved for installation and

2. Energy costs.

3.1. DARS-Ferrite Recovery process :

This process was developed with the sole idea of saving capital costs with respect to the causticizing step. Here the fuel energy used in reburning of lime is reduced. The first commercial installations of the DARS process for wheat/straw mill of 50000 tpd has been installed in Denmark.⁶ The accumulation of silica in ferric oxide loop is controlled by continuous purge of the finest dust fraction. It has been shown that the ferrite can be recycled upto six times even in case of bagasse black liquor.⁷ It is to be expected that for rice straw

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black liquor which has a large proportion of silica the number of cycles may come down. Further, since the organics to inorganics ratio drops down at each cycle its implications on combustion problems and requirements of auxiliary fuel are yet to be evaluated. The capital cost is claimed to be lower than 30% due to the elimination of the causticizing step. Although it does appear to have better prospects for small paper mills of 30 tpd capacity a number of factors like the influence of silica and the capital cost involved are yet to be evaluated in detail.

3 2 Wet Cracking System :

This process is modified version of Wet air oxidation process developed in Peoples Republic of China.8 The interesting aspects of this process are that they can function even in case of black liquor concentration as low as 10% solids This can eliminate multiple effect evaporator as rice straw liquor with good washing system produce liquor of 10% solids. All probof silica, viscosity etc. are completely lems avoided since there is no evaporation or combustion involed. It is claimed that the capital cost needed for putting up a wet cracking system could be only 50% of what is required for a conventional chemical recovery system. However, though no smelt is produced during the process, hazards due to explosions are to be anticipated and tackled as the system operates at about 1400 psi (20 MPa.)

3.3 Organosolv Pulping :

This process has been developed with agro-based raw materials in mind and is accordingly more suited for raw materials like bagasse, rice straw and bamboo rather than other hardwoods because of the lower carbohydrate and lignin content of the former. The Alcell process, the simplest approach to Orgonosolv pnlping has also developed a recovery processes for lignin and carbohydrate and these are marketed as animal feed⁹. Alcell lignin is a low molecular weight biodegradable material and thus is highly amicable to anaerobic treatment and can also be used as binder in wood panels. Solvent pulping carried out on the rice straw has been reported to give higher screen yield at even higher Kappa number for an alkali charge as low as 6%.10 Though chemical recovery is yet to be developed for this Organsolv pulping, the spent liquor from this pulping process has a much lower pollution load in terms of sodium, lignin and colour.

3.4 Membrane Technologies :

The application of membrane process-Ultrafiltration and Reverse Osmosis-for the treatment of black liquor has attracted the attention of a number of workers since the last two decades.¹¹ This process aims at the separation of higher molecular weight fraction containing most of the lignin, colouring compounds and bound soda by ultrafiltration and concentration of sodium compound in permeate by subjecting them to Some of the advantages are the Reverse Osmosis. elimination of evaporation and combustion and the possibility of causticizing only the RO concentrate. But the shortcomings are the UF concentrate still contains some fraction of lignin and sodium and these are lost and might also pose disposal problems. The overall chemical recovery is low since nearly 25% of soda compounds present in the black liquor are bound to high molecular weight lignin fractions which are lost in the UF concentrate.

The most critical factors for membrane technology to become economically viable is determined by a degree of fouling, the flux rate and the replacement cost of the membranes. Even with the excellent pretreament by microfiltration, fouling is expected to be so severe that it will reduce the flux within a few hours of operation. In case of silica rich liquor the fouling will be further aggravated by precipitation of silica which occurs as active alkali concentration gets depleted in the UF cencentrate. With the advent of high temperature membranes, flux can be significantly improved and probably by the selection of suitable membrane material fouling can also be controlled.

Most of the low temperature membranes available in India are of the cellulose acetate composition, which are not suitable for the above process. It might take quite some time for special polymer membranes to be manufactured in India These membrane technologies can also be adopted by even the big paper mills.

3.5. Gasification Process:

A new black liquor gasification process is being developed and it promises to have great potential as an economically viable chemical recovery system for small paper mills including those based on rice straw Demonstrated as pilot scale and personally witnessed by the author, this innovative indirect fluid-bed gasification has shown ability to handle black liquor at 30% solids concentration and yield a residue of 98% Na, CO_3 in the form of a dry powder. Since no smelt is produced and no pressure parts are involved, this process is operationally risk free compared to Smelters and Wet cracking process. Further since pre-evaporation is required to be done only up to 30% solids concentration and no combustion is involved, problems of silica are avoided, as silica gets purged with lime sludge after causticizing. The process claims that the product gas of calorific value 300 BTU /cu. ft. can be recycled to provide the necessary heat for gasification and does not require support of auxiliary fuel at feed concentration of 30% black liquor solids. Since product gas is scrubbed to absorb sulfur gases and air used is comparatively lower, emission standards in respect of SO₂ and NO₂ are easily met.

The potential advantages of this process such as smelt free operation, ability to handle rice straw liquor and the modular design to suit pulp mills of 15 tpd capacity, render this system as the most appropriate and economically viable system for small paper mills.

3.6. Chemrec Process.

This new process is bleieved to have the potential to revolutionize the entire recovery process and has been developed in Norway.¹² This process is radically different compared to the conventional process and involves pyrolysis rather than simple combustion of black liquor. As compared to the conventional boiler where in the black liquor is evaporated an simply burnt, the Chemrec process devides the recovery into two stages.

After evaporation, the liquor passes through a plasma reactor. Here it is heated to around 1000'C and ignited by an electric spark in an atmosphere which contains insufficient oxygen to support complete combustion. The organic matter decompose into carbon monoxide and hydrogen rather than into carbon dioxide and water. These gases are then burnt for the production of steam or for running gas turbines. A normal smelt of sodium sulphide and sodium carbonate is left in the reactor and these can be reused as normal. Installation costs are believed to be much less compared to the conventional process. The new process is supposedly safer, and more environment friendly by virtue of their lower emissions.

3.7. Biopulping.

The use of microbes in primary pulp manufacture is broadly referred to as Biopulping. It is based on the ability of the white rot group of fungi to colonize and rapidly degrade the lignin in the raw material. Extensive research' work is being carried out in different part of the world to exploit this technique. Some of the leading institutions were considerable advances have been made include STFI at Sweden, Biopulping consortium at Forest Products Research Laboratories at USA, Tuscia University at Itali, Guanghzhou Institute in China. Fungal pretreatment of the raw material reduces the residual lignin content and there by a lower chemical charge itself will be sufficient during the pulping process. However commercial exploitation of this process is still a long way to go. Preliminary studies carried, out by us in our laboratory¹⁸ indicated that the chemical change required during pulping can be reduced by more than 25% by preferential pretreatment.

4. Conclusions And Promising Options.

Small paper mills which produce less then 5000 tpa of chemical pulp are going to continually face the problem of chemical recovery and the accompanied pollution abatement problems as none of the known recovery systems can be installed by them due to technical and economical viability. As on date this is likely to include about 200 mills.

Of all the emerging technologies, the Gasification process seeme to hold the best commercial prospects as a part of the chemical recovery syslem. It is claimed that this system can be applied to mills of "any capacity" due to their modular construction. But the rest of the system (evaporator+causticizing) appears to be the limiting factor. This gassification process can solve the recovery and accompanied pollution problem of around 100 mills covering the above mentioned category of mills. In addition this process can be efficiently applied to sludge, effluent, wet pith etc. DARS process seems to be an attractive option for bagasse based mills of 30 tpd.

The existing big mills, desirous of introducing a new pulping line based on straw or bagasse, (to augment their wood/bamboo supply) have to expand the capacities of evaporators because of the low concentration of spent liquor from these agro-based raw materials. Since the gasification process accepts feed at concentration around 30%, evaporator capacity need not be increased and hence capital cost additions can be contained.

Membrane technology can be more gainfully employed for recovering chemicals from spent liquor from CTMP/CMP stages. A screw press can be used to squeeze out residual liquor to obtain a reasonable level of solids concentration (4-8%). This is subsequently prefiltered in a cartridge filter and processed by Ultrafitration to recover ligno-sulfonates, which can be sold or incinerated. Detailed work carried out in a pilot plant in canada has shown BOD reduction of 60%. Colour is also expected to be removed. The high flux rates obtained even at elevated temperatures is indeed encouraging. Further developmental work need to be done in this area.

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MERITS AND DEMERITS OF THE VARIOUS PROCESSES RECOMMENDED FOR SMALL PAPER MILLS

		Merits		Demerits
1. DARS Process	a)	Replaces recausticizing and thus reduces the fuel consumption	a)	The Organics to Inorganics ratio drops with each cycle
	b)	The Ferrite produced can recyc- led upto six times.	b)	Influence of silica is yet to be eva- luated
	C)	30% cheaper than other con- ventional process		
2. Wet cracking	a)	Can functio at very low black liquor concentrations	a)	System operates at very high pressure 1400 psi (20 MPa)
	b)	No evaporation or combustion is involved		ан на м
	c)	No smelt is produced during the		
3. Orgonosolv process	a)	process The lignin and the carbohydrates		 March 1997, and 1997 and 1 and 1997 and 1997 and 1997 and 1997 and 1997 and 1997 and 1997 and 1997 and 1997 and 19 1997 and 1997 and 1
	-,	produced during the process can be recovered and marketed		
	b)	The lignin recovered has a low molecular weight and hence is easily biodegraded.		
4. Membrane processs	a)	Eliminates evaporation and combustion	a) b)	The concentrate still carries lignin and Sodium and thus may pose dis- posal problems
	b)	Only the RO concentrete re- quires recausticizing.	b)	The overall chemical recovery is very low.
		n an the second s	c)	Fouling of the membrane and the consequent reduction in flux is very frequent
			d)	
5. Gasification Process	a)	Can handle solids as low as 30%.		
n de la composition de La composition de la c	b)	Yield a residue of No ₂ CO ₃ (98% pure) in the form of a dry powder.		en e
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 B. Hard S. H. Starter, Market Market, Market S. Starter, and Market Market Market Sciences, 2010. M. S. Santara, Santa	c)	No smelt and no pressure parts are involved.		
 Bondal de la servicia de la composición de la compo de la composición de la composición	•	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids.		
	•	No smelt and no pressure parts are involved. Evaporation needed to reach only		
	d)	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids. At 30% Black liquor solids no auxillary fuel is required.		
5. Chemrac Process	d) e)	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids. At 30% Black liquor solids no auxillary fuel is required. Modular design so as to suit the size of the small mill. Involves Pyrolysis rather than		
5. Chemrac Process	d) e) f)	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids. At 30% Black liquor solids no auxillary fuel is required. Modular design so as to suit the size of the small mill. Involves Pyrolysis rather than conventional simple combustion. Divides the recovery into two stages.		
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5. Chemrac Process 7. Biopulping	 d) e) f) a) b) c) a) 	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids. At 30% Black liquor solids no auxillary fuel is required. Modular design so as to suit the size of the small mill. Involves Pyrolysis rather than conventional simple combustion. Divides the recovery into two stages. A normal smelt sodium carbo- nate and sodium sulphite is left. Pretreatment cost are minimal		
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	 d) e) f) a) b) c) a) 	No smelt and no pressure parts are involved. Evaporation needed to reach only 30% solids. At 30% Black liquor solids no auxillary fuel is required. Modular design so as to suit the size of the small mill. Involves Pyrolysis rather than conventional simple combustion. Divides the recovery into two stages. A normal smelt sodium carbo- nate and sodium sulphite is left. Pretreatment cost are minimal Delignification occurs by a natu-	· · · · · · · · · · · · · · · · · · ·	

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