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EVALUATION OF TECHNOLOGIES ON RECOVERY OF BLACK LIQUOR CHEMICALS FOR SMALL AND MEDIUM SIZE PULP MILLS USING NON - WOOD FIBROUS RAW MATERIALS

Consultant

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LIST OF ABBREVIATIONS

a	- per annum (per year)
ABIPC	- Abstract Bulletin Institute Paper Chemistry (USA)
Al	- Aluminium
APPITA	- Australian Pulp and Paper Industry Association
BDMT	- Bone dry metric tonne
B.L.	- Black liquor
BOD	- Biological oxygen demand
BPR	- Boiling point rise
°C	- Celsius centigrade
Ca	- Calcium
$Ca(OH)_2$	- Lime
$CaSiO_3$	- Calcium silicate
Cl	- Chlorine
COD	- Chemical oxygen demand
CPPRI	- Central Pulp and Paper Research Institute, Saharanpur, India
CTAPI	- China Technical Association of Paper Industry
DARS	- Direct alkali recovery system
DBP	- German patent
DF	- Dilution factor
DR	- Displacement ratio
DS	- Dry solids
e.a.	- et alia (and other authors)
e.g.	- for example
FC	- Forced circulation evaporator
FF	- Falling film evaporator
FFF	- Free falling film evaporator
GJ	- Giga Joule
h	- hour
HDPE	- High density polyethylene
HHV	- High heat value
HNL	- Hindustan Newsprint Limited

INR - Indian Rupies (Indian currency)
INWFPPC '88 - 1988 International Non-Wood Fibre Pulping and Papermaking Conference Beijing, July 11 - 14, 1988
INWFPPC '92 - 1992 International Non-Wood Fibre Pulping and Papermaking Conference Shanghai, April 6 - 9, 1992
IPDT - Integral Procedural Decomposition Temperature
IPPTA - Indian Pulp and Paper Technical Association

K - Potassium
K_2CO_3 - Potassium carbonate
KOH - Potassium hydroxide

LHT - Liquor heat treatment
LHV - Low heat value
LP - Low pressure steam
LTV - Long tube vertical evaporator

Mg - Magnesium
MEE - Multiple effect evaporators
Mn - Mangan
MP - Medium pressure steam
MPa - Mega Pascal
MTCI - Manufacturing and Technology Conversion, Inc. (USA)
MW - Mega Watt

Na_2CO_3 - Sodium carbonate
NaCl - Sodium chloride (ordinary salt)
Na_2SiO_3 - Sodium silicate
NaOH - Caustic soda
Na_2SO_4 - Sodium sulphate
Na_2SO_3 - Sodium sulphite
NPE - Non-process elements

P - Phosphorus
PPI - Pulp and Paper International (Journal)

RAA - Residual Active Alkali as Na_2O
RMB - Yuan Chinese currency
RPM, rpm - Revolutions per minute

SBR - Submersed bubble reactor
SIDA - Swedish International Development Agency

SiO_2 - Silica
SS - Stainless steel
SS - Suspended solids
STV - Short tube vertical evaporator
SVR - Swollen Volume Ratio

t - tonne (metric, 1,000 kg)
TAPPI - Technical Association of Pulp and Paper Industry (USA)
TCCR - Thermo Chemical Conversion reactor
TDS - Total dry solids of black liquor

TIG - Temperature of ignition
TPD - Tonnes per day

UNDP - United Nations Development Programme
UNIDO - United Nations Industrial Development Organization
USD - United States of America dollar
USP - United states patent

WAO - Wet air oxidation
WBL - Weak black liquor

SUMMARY

1. The objective of this study was to critically evaluate equipment and technologies available in China, India, Europe and USA, on recovery of chemicals from non-wood, especially agro-residues black liquors in small and medium size pulp mills (50 - 200 TPD). Existing small scale recoveries were reviewed and all sub-processes evaluated. A pre-feasibility calculation of medium concentration black liquor incineration in recovery boilers and low concentration black liquor (B.L.) in fluid bed reactors has been carried out. The waste (black) liquor from small and medium size pulp mills has to be treated to meet environmental regulations.
2. Agricultural residues contain considerable amount of dust, which increases silica content of raw material and impairs washing of pulp. Cleaning of agro-based fibrous raw material by the dry or wet process decreases silica content and improves washing.
3. Washing of non-wood pulp especially of straw pulp is more difficult, when compared with wood pulp. Washing equipment has a lower output (less pulp can be washed per unit wash area), the washing efficiency is lower (usually 85 - 90 %). This is resulting in low chemical recovery efficiency (75-80 % for wheat straw, slightly higher for bagasse B.L.) Black liquor is more diluted (concentration just 10-7 %). Consequently, less dry solids (DS) can be collected and incinerated and nearly twice more water per tonne pulp/DS has to be evaporated prior to incineration when compared with wood B.L. This reduces heavily overall thermal efficiency, i.e. net production of steam.
4. Conventional drum washers are generally used for washing of agro-based pulps. Comparatively good washing efficiency is obtained in bagasse pulp washing, but washing of straw pulp is more difficult. There are attempts to use horizontal wire washers with good results in bagasse pulp washing, but less satisfactory results in straw pulp washing. More development activities are required particularly in straw pulp washing.
5. Agro-residue B.L. properties are less favourable than of woof B.L. Viscosity is considerably higher resulting in lower heat transfer coefficient in evaporation (larger evaporating surface is required). High silica content especially of straw B.L. is causing heavy scaling of evaporators decreasing capacity and requiring frequent cleaning. Silica impairs also washing of pulp and causes deposits in recovery boilers.
6. High viscosity is limiting maximum attainable concentration of B.L. prior to firing resulting in less generated steam. High viscosity can be partly off-set by keeping sufficient residual active alkali in B.L. There are indications, that modification of alkaline cooking conditions e.g. kraft or low sulphidity cooking and addition of sodium sulphite can considerably reduce viscosity. B.L. heat treatment drastically reduces viscosity, but this is commercially used in a few

installations for wood B.L. only and is expensive.

7. Due to high viscosity and scaling tendency agro-residues B.L. evaporation in conventional rising film evaporators is limited to 40-45 % concentration even if forced circulation evaporator is used as 1st (concentrator) effect. In existing small mills usually 5 effect evaporator trains are installed, with one forced circulation body. In China some mills have installed falling film evaporators as 1st (concentrator) body. The B.L. is concentrated to firing concentration which is generally 52-53 % , on direct contact evaporators, usually cascade type. Some mills, mainly bagasse mills in South America, are concentrating to about 60 % prior to firing.
8. Falling film evaporators (tubular or plate type) are less sensitive to viscosity and less prone to fouling (scaling). It is adviseable to use these types especially as concentrators. There are indications that these type of evaporators and especially the recently developed modification (vapour recycling evaporator) will make it possible to increase B.L. firing concentration and, consequently, to increase thermal efficiency. However, this may be difficult with straw B.L. especially rice straw B.L. due to high silica content.
9. Combustion earlier caused problems due to deposits of silica and potassium salts. Modifications of recovery boilers, such as more generous spacing between boiler (economizer) superheater tubes, vertical configuration, screens to cool down flue gases etc., actually reduced these difficulties to minimum. Problems due to lower heat content of B.L. solids and lower firing concentration have been solved by modification of combustion air system and higher air temperature. To avoids black-outs small boilers usually use some fuel oil. This is not necessary in case or air cooled refractory smelter-boilers as in these considerably less heat is extracted from the hearth, than in waterwall (membrane wall) boilers. Calculation have indicated, that systems with firing at low concentration (52 - 53 %) and direct B.L. evaporating have a thermal efficiency well below 60 %. Indirect evaporation and increasing firing concentration to 60 % increases thermal efficiency of incineration to over 60 %.
10. The overall thermal efficiency of the recovery system, i.e. the net surplus of steam (steam generated minus steam for evaporation) is determined by the concentration of B.L. after washing and after evaporation. Systems with low weak black liquor concentration (say 7 %) and low firing concentration (52 - 53 %) have a steam deficit. As steam e.g. in India is expensive, such systems may operate with loss in case of low capacity (below 60-70 TPD pulp). This loss is caused also by high capital costs in case of low capacity.
11. A fluidised bed incineration system has lower investment cost. However, it is incinerating at low concentration (about 45 %) and thermal efficiency is lower, if no steam is produced. Such a system has higher operation costs per tonne of recovered caustic soda than the recovery boiler system. Consequently, production costs are higher.

12. The pre-feasibility calculation indicated, that the economy of chemical recovery is influenced mainly by
    - overall thermal efficiency, i.e. if a steam surplus is available
    - economy of scale
    - interest rate

    In a system with low weak B.L. concentration and low firing concentration the operating costs (direct costs) are high. At low capacity the capital costs are high and the system may operate with loss. At higher capacity (about 100 TPD pulp) the capital cost are lower and the system works with profit. Low interest rate (say 8 %) can considerably improve economy and even small systems may work with a profit.
13. High thermal efficiency systems (W.B.L. 10 %, firing 60 %) will work with profit even at 50 TPD pulp. However, this at present time is possible with bagasse only, and not with straw B.L.
14. Evidently recovery of bagasse B.L. is without serious problems and may be profitable at low capacities. Recovery of chemicals from wheat straw B.L. is possible, but due to difficulties may work with a loss at low capacity (below 60-70 TPD pulp). This is also the experience of some mills in China.
15. No rice straw black liquor chemical recovery is in operation at present time, except using a mixture of 30 % rice straw and 70 % wheat straw in a small pulp mill in China. Difficulties are expected in washing and due to silica content especially in evaporation. Situation may be improved by desilication of B.L.
16. Desilication of bamboo kraft black liquor was tested in industrial scale and no appreciable difficulties are expected with agro-residues black liquor. Two pre-feasibility calculations have indicated, that desilication may work with profit only if separated silica is marketed for a good price and the capacity is not below 100 TPD pulp. More development work may be required to improve economy of this process. A large-scale desilication plant for bamboo B.L. is planned in India, but no plant is in permanent operation at present. Dry or wet cleaning or combined dry and wet cleaning of agricultural residues fibrous raw materials can also reduce silica content considerably and improve evaporation of black liquor.
17. Due to high silica content no lime reburning is possible without desilication of straw B.L. Some bagasse mills are reburning lime mud, but 15 to 50 % of lime mud is purged to keep silica content in acceptable limits.
18. Chemical recovery is the best pollution abatement process. As chemical recovery in very small mills (below 60-70 TPD pulp) especially from straw B.L. may not be profitable a pre-feasibility calculation compared black liquor recovery with black liquor biological treatment :
    - when compared a B.L. recovery working with loss with an activated sludge treatment at same level of interest on capital, than the loss / expenditure for B.L. processing is less in case of B.L. recovery. However, investment cost is considerably higher for B.L. recovery. Moreover,

activated sludge treatment does not eliminate all polluting agents, just BOD causing substances. Recovery eliminates at least 90 % of all polluting substances;

- anaerobic treatment utilizes a part of organic matter to produce methane gas. It eliminates about 80-90 % of BOD but COD about 50 % only. All lignin and inorganic salts are remaining in effluent. Anaerobic treatment operates with a profit, the pay-back period is about 6 years. Such a system is several years in operation in a 40 TPD bagasse pulp mill in India.

19. Emerging organosolve processes may be a viable alternative to alkaline pulping of agricultural residues as some of these processes are based on extractions of lignin by solvent as ethanol, for example, which is recovered in a closed system through a distillation tower and lignin is separated. In this case no incineration in recovery boiler is required and silica problems may be avoided. Most of these processes have been tested in pilot/demonstration scale but currently none is in industrial operation.
20. To improve efficiency and economy of chemical recovery in small and medium size pulp mills based mainly on agricultural residues the following development work is recommended :
    - improvement of washing by optimization of particularly horizontal washers
    - investigation of B.L. viscosity reduction by modification of cooking conditions
    - testing of modern falling film evaporators to achieve high concentration B.L.
    - to investigate possibility of simplification and price reduction of desilication system. To promote marketing of separated silica
    - to test new pulping processes.

It is recommended to organize cooperation of various research institutions, machinery companies and mills and if possible to support a demonstration plant.

1. INTRODUCTION

1.1 General Situation

More than 90 percent of the world pulp production is manufactured from wood in large scale pulp mills (200 to about 1,000 BDMT/day). However, in developing countries more than 50% of the pulp is manufactured from non-wood materials, mainly from agricultural residues (bagasse, rice and wheat straws) but also from bamboo and from various grasses. Most of the pulp mills using agricultural residues are of small and medium size (30 to 200 BDMT/day) and are using the alkaline pulping process (soda or kraft). While all wood based alkali pulp mills are incinerating the spent liquors from pulping (black liquor) and recovering the pulping chemicals (caustic soda and sodium sulphide) most of the small agro-based pulp mills are using the soda process (pulping with NaOH) and are draining the spent liquor from pulping resulting in heavy water pollution and loss of chemicals. Most non-wood small and medium size pulp mills are in China and India.

1.2 Current situation of the pulp and paper industry in China and outlook for the year 2000

The paper industry in China was increasing production in 1994 by 14,5%. The average growth rate in the years 1990-1994 was 11,8%. The total paper and board production in China in 1994 was 21.38 million tonnes. There are about 6,000 paper mills in China. Out of these about 1,600 are owned or under supervision/administration by the state. The paper and board production of these mills in 1994 was 8.98 million tonnes i.e. 42% of total production. 58% of the total production was manufactured in medium and small size mills mainly by township enterprises. There are several large scale projects of state enterprises which should strengthen the position of the state enterprises in the pulp and paper industry. Nevertheless the small and especially medium size pulp and paper mills will continue to play an important role. In 1994 the total production of pulp was 15.89 million tonnes. Out of this only 1.0 million tonnes was wood chemical pulp and 0.5 million tonnes wood mechanical pulp. 1.6 million tonnes was imported. It is expected, that wood pulp production will increase. Availability of wheat straw may decline as a result of technological change in agriculture (implementation of combine harvesting). Nevertheless non-wood fibres (including reeds) will continue to be the most important fibrous raw material in China.

In China only 81 pulp mills have chemical recovery. Out of this about 20 are using non-wood fibrous and are of small to medium size (max. 150 BDMT per day). The total caustic soda consumption in the pulp and paper industry in China in 1994 was about one million ton. The total caustic soda recovered in 1994 was 355,300 t/a i.e. under 40% of total caustic soda used, even if recovery increased by 1.9% as compared to 1993.

The small and medium size pulp mils face serious environmental problems as well as difficulties with wheat straw supply. About 100 small and medium size pulp and paper using non-wood fibrous have been shut down due to unsolved pollution problems. A new mill in Shanghai was never commissioned due to environmental limits as well as due to shortage of wheat straw.

Implementation of chemical recovery in non-wood pulp mills is an issue of survival as pollution limits are getting more stringent and also due to the economical situation. Prices of raw materials are increasing by 60 to 100% but prices of paper are not increased in line with prices of raw materials. The price of caustic soda (as 100%) is at present time in various part of China RMB 1,500 to 1975 (USD 185 to 224). As a result a number of mills are in deficit. It is necessary to introduce more economically and technically feasible chemical recoveries.

1.3 Situation in India

Small pulp and paper mills are typical for India. Medium and large scale pulp mills are using forest based materials (bamboo, hardwoods, eucalyptus) and only the new big newsprint mills are using bagasse. Small pulp mills are using agricultural residues (bagasse, wheat and rice straws) and various grasses. However, the percentage of small pulp mills and their share in total production is lower than in China. In India about 40-45% of total pulp production is manufactured in small, agro-based pulp mills. The total production of pulp in India in 1993-1994 was about 1.4 million tonnes, the paper and board production about 2.5 million tonnes. The estimate for the years 2000-2001 are between 3.8 to 4.5 million tonnes. This will require substantial increase of pulp production as well and it is expected, that small pulp mill will continue to play an important role. However, small pulp will face serious difficulties. The price of caustic soda increased to INR 15,000-18,000 per ton. In 1994 the Indian Government imposed and excise duty of 10% on papers made from bagasse and other agricultural residues, while the tax on forest based production has been reduced to 20%. Paper mills based on bagasse and agricultural residues had been exempt from excise duties for several years. This economic pressure resulted in closure of several small pulp mills (68 out of 297).

Simultaneously the environmental limits and regulations are getting more stringent. Evidently the small mills have to introduce chemical recovery in order to reduce production cost and meet the more stringent environmental limits. This changed the situation in India. Whereas in 1993 there was no small pulp mill with recovery (in contrary to China), in 1995 already two recoveries are in operation and another 4-5 are ordered or on stream. The activity of Indian equipment manufacturers also increased.

1.4 Objectives of this study

The objective of this study is to review the information available in UNIDO (1 - 11) and technical journals on recovery of chemicals from non-wood black liquor including desilication as well as evaluate the equipment and technologies available in Europe, USA, China and India. The evaluation should include all sub-processes of chemical recovery including efficiency (thermal and chemical) and possibility of steam/electricity co-generation as well as estimated investment and operation costs.

It should be mentioned, that the wood and straw pulp mills in Europe and USA at the end of 19th and beginning 20th century were of small capacity (25 to 100 TPD). The mills using an alkali cooking process (soda or kraft) had a simple chemical recovery. Earlier batch incineration of black liquor in pans was used. Later black liquors (from both wood and straw pulping) were continuously incinerated in a refractory lined conical rotary roaster. The black ash containing carbon from organic substances and soda ash was leached and the soda solution causticized with lime (CaO). The rotary roaster was soon combined with a moveable smelter, where the carbon from black ash was incinerated and sodium sulphate of the kraft black liquor reduced to sulphide. The smelt was dissolved and causticized. Such an equipment is shown on Fig.1 . The roaster, which could incinerate black liquor from manufacture of 25-30 TPD pulp had a diameter of 3 m and length 6-7 m. Later a waste heat boiler was added. The chemical and thermal efficiency was low (about 50-60% and 50% respectively).

A new modern recovery boiler (Fig.2) can incinerate up to 3,300 tonnes of dry solids per day. In such a boiler incineration, smelt generation including sodium sulphate reduction and steam generation is combined in one space. The thermal efficiency is more than 65%. The height of a very large scale boiler may be 50-55 m.

The development objective in this field is scaling down and modification of the highly effective large scale recovery system to the scale of small a medium size mills taking into consideration reasonable investment costs and properties of black liquors from pulping of non-wood fibrous raw materials. This study evaluates from these points of view all sub-processes of a recovery system.

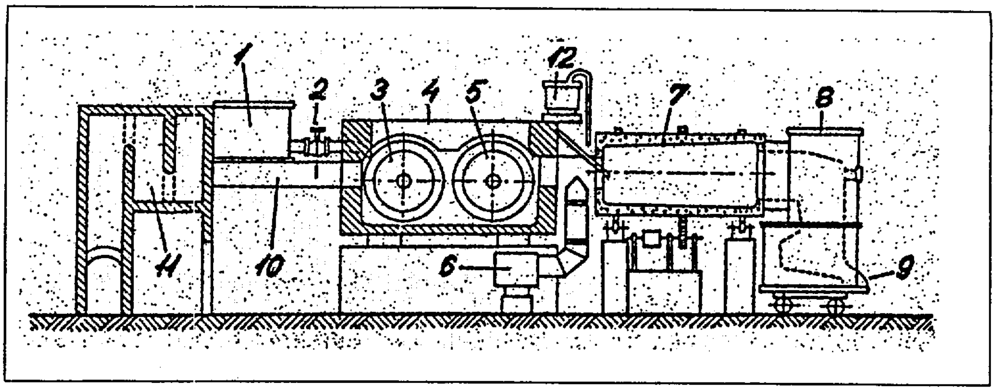


Fig.1
OLD TYPE ROTARY ROASTER
WITH REMOVABLE SMELTER

1. B.L.tank
2. Pipe
3,4,5. Disc evaporator
6. Suction pump
7. Rotary roaster
8. Smelter
9. Outled
10. Duct
11. Flue gas chamber

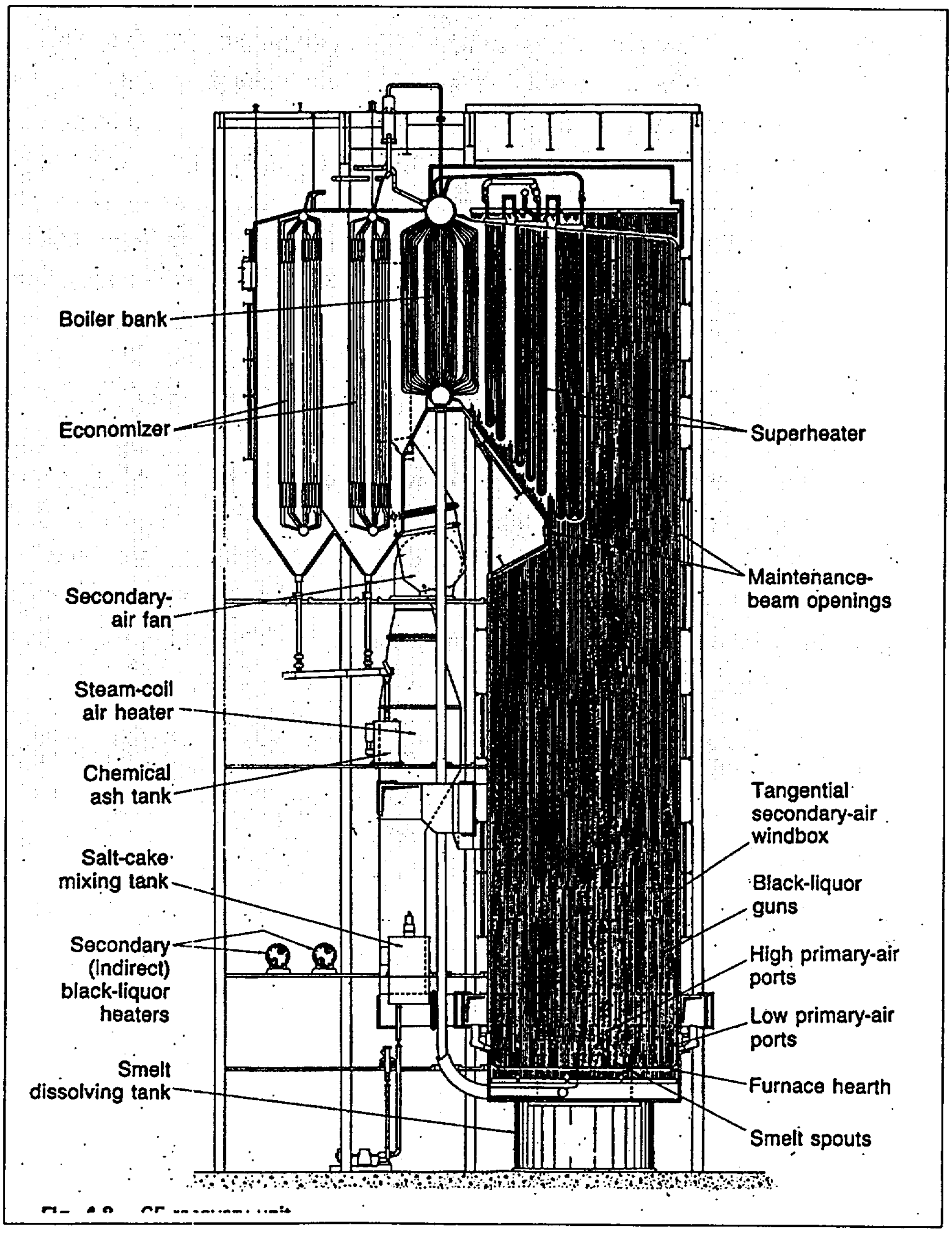


Fig.2
MODERN RECOVERY BOILER
Source /20/

2. PROPERTIES OF FIBROUS RAW MATERIALS AND BLACK LIQUORS

2.1 Chemical composition of fibrous raw materials

Lignin content of main non-wood raw materials is in the range 13 to 30% (Table 1). Wheat and rice straw has a low lignin content.

Table 1

PRESENCE OF LIGNIN AND SILICA IN FIBROUS RAW MATERIALS IN %

	Silica	Lignin
Wood	Traces	18 - 29
Bamboo	0.6 - 3.5	22 - 30
Bagasse	1.1 - 2.5	18.5 - 25
Reed	2.0 - 3.0	21
Wheat straw	3.0 - 7.5	16 - 18.5
Rice straw	8.0 - 12.0	12 - 14

Source (6a, 17, 18, 23a)

Consequently the polysacharide content of bagasse and especially in wheat and rice straw is higher, than in wood and more polysacharides and polysacharide-lignin complexes are dissolved in pulping resulting in high viscosity of black liquor (24).

Ash and especially silica and potassium content in non-wood raw materials is high (Table 1). The content of these components is in a wide range depending on variety and soil conditions. Data of raw materials in China are in Table 2 and of Indian raw materials in Table 3.

Table 2

SILICA CONTENT IN DIFFERENT SPECIES IN CHINA

	Rice Straw	Wheat Straw	Reed	Bagasse	Bamboo	Pine
Silica (%dry material)	11.27	6.77	3.09	2.02	0.62	-
Ash (%dry material)	14.38	7.89	3.78	2.38	1.52	0.20
SiO_2 (%B.L. dry solids)	5.8	7.48	2.66	2.38	0.52	0.21

Source(21)

Table 3

SILICA AND POTASSIUM CONTENT OF INDIAN RAW MATERIALS					
	Bamboo	Bagasse		Rice straw	Wheat straw
		A	B		
Ash %	4.05	2.20	3.50	18.40	7.20
Silica %	3.0	1.11	1.80	11.80	3.20
Potassium %	ND	0.61	0.06	0.87	0.65

Source (16) NO - Not determined

There is a significant difference between Indian and Chinese bamboo with regard to ash and silica content. Low ash and silica content has also *Bamboosa vulgaris* from North Brazil (unpublished data by author):

	Stem	Branches
Ash %	0.98	1.57
Silica %	0.29	0.48

Higher ash content in leaves of straw is reported by Wurz (17). Silica content is influenced by soil contamination. Washing of bamboo chips and straw can reduce silica content by 50% (6b, 22).

2.2 Silica and potassium in black liquors

Silica has a negative impact nearly on all chemical recovery sub-processes. The silica content in black liquors is in a wide range depending on silica content in raw materials and cooking conditions. The distribution of silica between the pulp and black liquor in rice straw cooking under various conditions in laboratory scale is presented in Table 4:

Table 4

INFLUENCE OF PULPING CONDITIONS ON THE DISTRIBUTION OF SILICA BETWEEN PULP AND BLACK LIQUOR			
Cooking process	Cooking temp. °C	Pulp ** %	Black liquor ** %
Soda (8% NaOH)	160	64.6	35.4
Soda (10% NaOH)	160	54.3	45.7
Soda (12% NaOH)	160	25.0	75.0
Soda (10% NaOH)	140	49.0	51.0
Carbonate (12%) *	160	72.5	27.5
Alkaline sulfite	160	73.5	26.5

* 12% NaOH (40% NaOH + 60% Na_2CO_3)
** Percentage of total silica in raw material

Source (6a)

Evidently increasing alkali charge increases the portion of dissolved silica. In carbonate pulping, where NaOH concentration is low, silica dissolution is also low. These conditions are in the NACO process (22). In China frequently sodium sulphite is added to the white liquor. This is suppressing silica dissolution as shown in Table 5. Silica and potassium content in mill black liquors from various raw materials in India is indicated in Table 6.

Table 5

SILICA CONTENT IN BLACK LIQUOR SOLIDS (CHINESE MILLS)				
	Wheat straw		Rice straw	
Chemical charge % NaOH	17	13	11	7
Na_2SO_3	-	3	-	3
SiO_2 in B.L. dry solids %	1.86	1.19	3.57	1.83
Viscosity at 20°Be',20°C [mPa.s]	72	36	207	93

Source(23b)

Table 6

SILICA AND POTASSIUM IN MILL BLACK LIQUORS (INDIA)				
Mill Raw Material	pH 30°C	RAA g/l NaOH	Potassium % on TDS	Silica SiO_2 % on TDS
1. Bagasse	11.9	7.3	3.1	3.75
2. Bagasse	10.0	0.4	0.4	0.80
3. Bagasse	10.7	0.4	0.5	2.20
4. Rice straw	9.6	0.16	0.2	1.97
5. Rice straw	9.8	0.64	7.9	3.69
6. Rice straw	6.3	Nil	3.6	12.85
7. Wheat straw	7.8	Nil	4.5	6.30
9. Grass based	11.5	3.3	4.1	4.16
10. Grass based	7.3	Nil	2.1	1.63

Source(5)
1 - Mill equipped with chemical recovery system
TDS - Total Dissolved solids
RAA - Residual Active Alkali
2-10 - Mills without chemical recovery

Table 6 indicate, that silica content is dependent generally on residual active alkali at the end of cooking. The more the RAA the higher the silica content. Recycling of chemicals in a mill with recovery also increases silica content in black liquor (compare mill 1 and 2-3). However, other factors also influence silica content in black liquor. An extremely high silica content in mill No.6 may be a result of rice straw contaminated with dust and soil. Generally the silica content in straw B.L. is up to 5% on TDS.

Potassium content is higher in straw and grass black liquors as compared with bagasse B.L. However, in the bagasse mill with chemical recovery (mill No.1) the potassium content is higher, due to accumulation of potassium through recovery of chemicals.

Very few data are available about chlorides content in agro-based raw materials and black liquor. In two mills in India 0.2 (bagasse) and 1.67% chlorine on TDS (rice straw) was determined. In laboratory cooking of wheat and rice straw the chlorides content was 0.65 and 0.79% on TDS respectively (5).

It is noted, that black liquor composition and especially silica and potassium content varies in a wide range depending on raw material, raw material cleaning and cooking conditions. In mill without recovery of chemicals the tendency is to use minimum caustic soda. This of course, has negative impact on pulp properties and bleaching chemicals consumption as Kappa No is high. Once a chemical recovery is installed there will be a tendency to use higher alkali charge and silica content in B.L. will increase. This should be tested and considered when planning a chemical recovery.

2.3 Viscosity of black liquors

It is well known, that viscosity of agricultural residues soda pulping black liquor is significantly higher, than of wood black liquor. This is result of the higher molecular weight of lignin and higher hemicellulose content in agricultural residues soda black liquors as hemicelluloses are less degraded than in wood black liquor (24). The viscosity versus total dissolved solids content for various black liquors is shown in Table 7 (5). This shows the difference between hardwood and bamboo black liquor on one side and agricultural residues soda pulping black liquor on the other side.

Table 7

VISCOSITY OF DIFFERENT SODA BLACK LIQUOR

Particulars / Total solids	Viscosity [mPa.s] at 80 °C at different solids concentration			
	35 %	40 %	45 %	50 %
Rice straw	75	136	325	1,000
Wheat straw	57	118	300	886
Bagasse	44	91	240	885
Bamboo *	16	40	72	185

Source (5) * Kraft B.L.

Chinese authors (23c) claim a much larger difference in viscosities between non-wood fibre black liquors and wood black liquors. According these authors at low concentrations the difference is 2-3 times higher and at high concentrations 20-30 times higher. The viscosity decrease is in following order of black liquors :
chinese alpine rush - rice straw - wheat straw - reed - bamboo - cotton stem - wood - reed rayon pulp at same dry solids concentration.

In fact data presented by various authors differ significantly which may be a result of different raw materials properties but also due to different experimental conditions. More systematic research and testing is required using standardized experimental and testing methods.

2.3.1 Influence of cooking process

Viscosity of black liquor from the same raw material prepared by laboratory cooking is shown in Table 8. Kraft, soda - antraquinone and alkali sulphite process B.L. have significantly lower viscosities when compared with soda B.L. Additions of sodium sulphite is successfully applied in some Chinese mills having chemical recovery (23b). A part of the make-up chemicals added to the white liquor is sodium sulphite which is after cooking in the incineration process reduced to sodium sulphide. These mills are actually using low sulphidity white liquor with addition of sodium sulphite. It is advisable to consider these alternatives when planning a chemical recovery system. Viscosity of bagasse black liquor from the Vindya (India) pulp mill using the soda-antraquinone method is shown in Table 9.

Table 8

VISCOSITY OF BLACK LIQUORS OF NON-WOOD MATERIAL FROM DIFFERENT PULPING PROCESSES (laboratory)

Pulping process	Soda		Kraft		Soda-AQ		Alkali-sulphite
	Viscosity [mPa.s]						
TDS %	80°C		80°C		90°C		80°C
	Bagasse	Rice straw	Bagasse	Rice straw	Bagasse	Rice straw	Rice straw
35	44	75	13	18	10	79	15
45	240	325	50	46	29	43	45
55	over 3,000		219	300	126	251	144

Based on CPPRI experiments

Table 9

VISCOSITY OF BAGASSE MILL BLACK LIQUOR

TDS	Viscosity [mPa.s]		
% w/w	82°C	90°C	104°C
35	15	10	80
40	23	16	12
45	40	29	21
50	79	56	41
55	213	126	91
60	741	500	263
63	2,571	1,977	1,121

Bagasse black liquor from Vindya mill (India).
Soda - antraquinone (0.05%) pulping. RAA as NaOH 4.33 g/l.
Tested by CPPRI

2.3.2 Influence of temperature

Viscosity of agricultural residues black liquors is strongly temperature dependent, more than of wood black liquors. The viscosity - black liquor dry solids concentration relationship for wheat straw at various temperatures is shown on Fig.3a (25) and the difference of viscosities between 80°C and 100°C for rice straw on Fig.4 (5). Handling of black liquors at high temperatures (pumping, flow through pipes to recovery boiler) will be limited by the boiling point, unless pressure systems are used.

The equation for viscosity-temperature relationship formulated by some authors (26,27) are valid for a certain type of black liquor. No general equation could be formulated. A useful method is to plot logarithm of viscosity against temperature. As this is in most cases approximately a straight relationship this can be extrapolated to higher temperatures at which direct measurement is difficult.

2.3.3 Influence of residual alkali (RAA)

Viscosity can be reduced significantly by keeping RAA at acceptable level. The viscosity RAA relationship for rice straw soda black liquor is shown for 80°C and 100°C on Fig.4 (5). Slightly higher RAA is required for wheat straw B.L. The viscosity - bagasse B.L. concentration relationship at various RAA is shown on Fig. 3b. Generally RAA level at least of 4-8 g/l should be maintained also for keeping silica in solution during evaporation of B.L. Higher RAA levels does not reduce viscosity.

2.3.4 Reduction of B.L. viscosity by thermal treatment

The maximum dry solids concentration in evaporation, pumping and spraying of B.L. into the recovery boiler is limited by viscosity, as pumping is possible up to 400-500 mPa.s only. For wood this limit is practically 65-67% TDS for simple systems, but is lower for black liquor from agricultural residues. Small and Fricke published in 1985 (28) and Söderhjelm in 1986 (26) the phenomenon of black liquor viscosity reduction by heat treatment. A more detailed study of heat treatment was presented by Ryham (29) and later marketed by Ahlström Company (Finland). There are at least two industrial application (see chapter - B.L. evaporation). Kulkarni (30) tested heat treatment of bagasse semi-concentrated bagasse black liquor (about 35% TDS). The reduction of viscosity shown in Table 10 makes it probably possible to evaporate bagasse B.L. to 70-75% TDS. According Kulkarni (30) the reduction of viscosity is a result of breaking up the large molecular mass of lignin-polysacharides complexes.

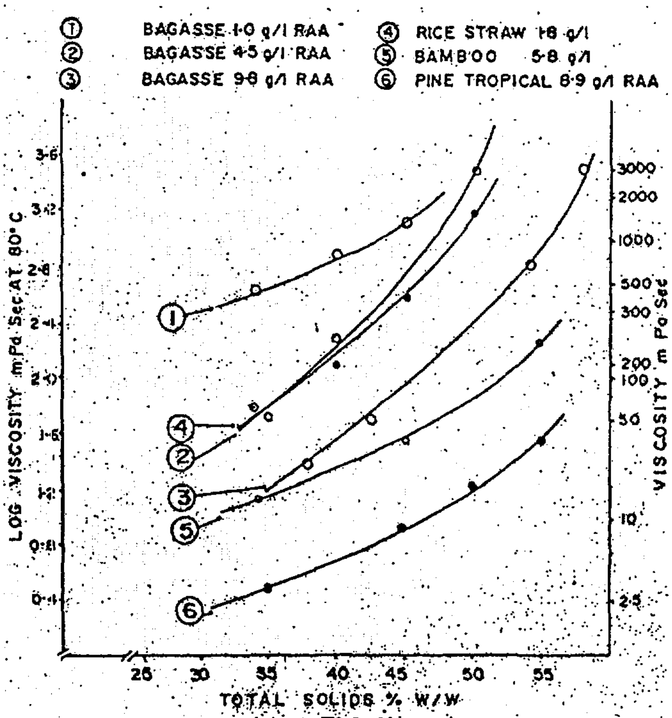


FIG.3b
VISCOSITY & TOTAL SOLIDS RELATIONSHIP OF BLACK LIQUORS FROM DIFFERENT RAW MATERIALS.
Source (24)

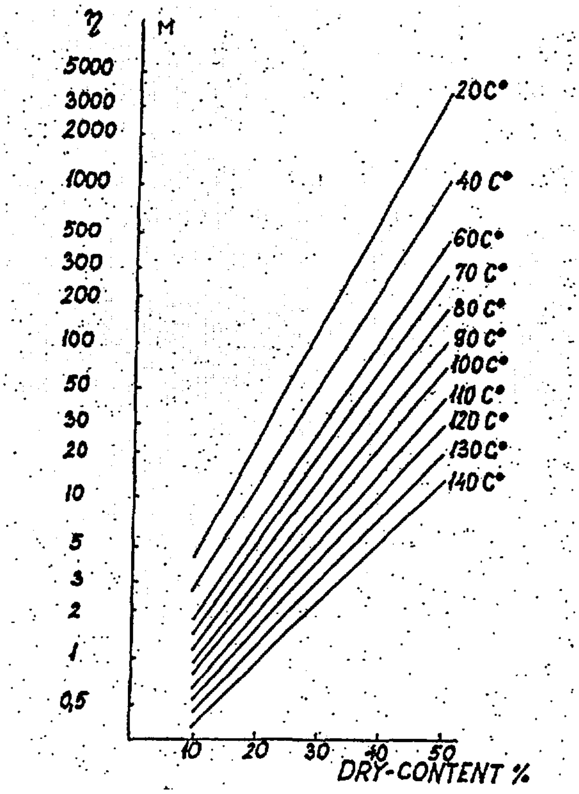
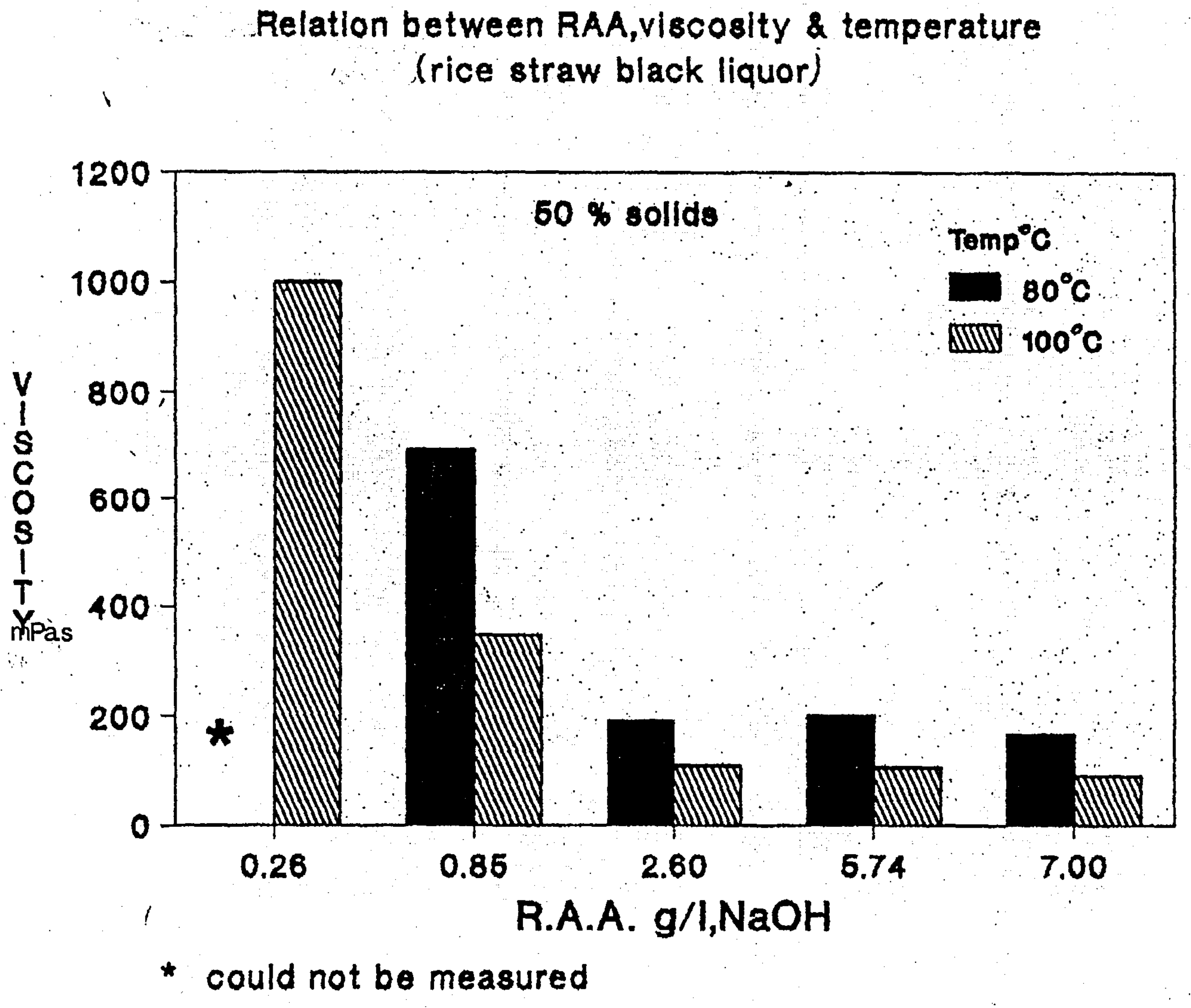


Fig. 3a
WHEAT STRAW BLACK LIQUOR VISCOSITIES
Source (25)



Relation between RAA,viscosity & temperature
(rice straw black liquor)

* could not be measured

Fig. 4

Viscosity reduction is accompanied by a slight decrease of heat value (HHV) - 3,110 kcal/kg from 3,420 kcal/kg TDS, but improvement of incineration properties - lower Integral Procedural Decomposition Temperature (IPDT), lower temperature of ignition (TIG) and higher svolen volume ratio (SVR). The technology and equipment for this process in discussed in the chapter "Evaporation".

Table 10

VISCOSITY OF BAGASSE BLACK LIQUOR BEFORE AND AFTER HEAT TREATMENT

	Viscosity at 90°C [mPa.s]	
TDS %	before HT	after HT
55	250	60
60	600	100
62	880	135
64	1,300	200
68	*	350

* Measurement not possible

Source (30)

2.4 Colloidal properties of black liquors

The colloidal stability of straw and bagasse black liquor decreases with decreasing pH. Black liquor especially from low alkali charge cooking has a tendency to form during storage a sludge with high silica content. This was proposed in China as a simple method of desilication (23d).

Another feature of colloidal instability is precipitate formation during evaporation of black liquor. Rice black liquor produces precipitate at about 27% concentration of TDS (30). This should be taken into consideration, when selecting suitable evaporator type. It was shown by Kulkarni (24), that high molecular weight lignin and presence of organic acids in significant portion are the reasons for colloidal instability.

Straw black liquor has a tendency to produce more foam, which has a negative impact on washing of pulp.

2.5 Thermal and incineration properties of black liquors

The high heat value (HHV) of dry solids of agricultural residues black liquor is generally 12.5 to 14 MJ/kg (2,990 to 3,350 kcal/kg dry solids) depending on raw material but heavily influenced by yield of pulp and chemical charge. Agricultural residues B.L. contains less lignin having higher heat value and more polysacharides and degradation products thereof having lower heat value. In contrary wood based black liquors contain more lignin and have higher heat value. The difference in heat value is however less as chemical charge and consequently ash content of agricultural residues black liquor is lower.

Elementary composition varies with yield and chemical charge (i.e. ash content). Data were published by Kulkarni (24, 33) and in a UNIDO report (5), but it is advisable always analyse elementary composition when calculating combustion conditions.

Swelling volume ratio (SVR) introduced by Oye (31) is the volume of one gram of black liquor after evaporation of water and swelling during volatile burning involving pyrolysis and gaseous combustion. It is actually the volume of char. The higher the SVR the faster the rate of thermal decomposition. SVR is generally lower for agricultural residues B.L. when compared with softwood indicating less favorable combustion conditions, but results of various authors differ significantly.

Thermogravimetric analysis gives a more accurate indication of combustion properties. The results of detailed CPPRI studies (23e, 24) are presented in Table 11. IPDT (Integral Procedural Decomposition Temperature) indicates temperature at which half of the dry solids are combusted. This is higher for agricultural residues B.L. when compared with wood B.L. Ignition temperature and ignition time is also higher for agricultural residues B.L. indicating that these black liquors are resistant to thermal decomposition and burn slowly when compared to wood black liquor.

Table 11

RESULTS OF THERMAL ANALYSIS OF BLACK LIQUORS

Sample	Carbon %	Organics %	IPDT * °C	Ignition Temp.(Tig) °C	Time of ignition
1. Bagasse B.L. (Mill)	39.9	69.5	574	722	84
2. Rice straw B.L.	39.6	79.2	588	662	71
3. Wheat straw B.L.	37.4	78.8	574	618	-
4. Hardwood (Mixed)	35.6	70.2	430	622	45

* Integral Procedural Decomposition Temperature (IPDT)
Temperature rise: 20°C/min.

Source (23e, 24)

3. NON PROCESS ELEMENTS IN THE RECOVERY PROCESS

Undesirable or non-process-elements (NPE) in the black liquor and alkali circulation system are potassium, magnesium, aluminium chlorine, iron silicon, manganese, magnesium and calcium. In the lime circulation system magnesium, aluminium, iron, manganeses silicon, sodium, potassium sulphur and chlorine are undesirable (32). K, Cl and Al have no distinct discharge point from the recovery system and under normal conditions tend to accumulate in the lime cycle. However Al may be discharged if reacting with SiO_2. Substances such as Ca, Mg, P, Mn and in case of non-wood pulping SiO_2 are removed from the alkali cycle and accumulate in the lime cycle. In non-wood pulping the most important NPE are silica, potassium and in some cases chlorine.

3.1 Influence of potassium and chloride on softening and melting point of B.L. inorganics

Potassium is present in appreciable quantities in agricultural residues B.L. The actual content varies in various locations due to different soil conditions and fertilizing level. Chlorides are present in agricultural residues in small quantities only, but may be introduced by water. The built up of these elements by recycling alkali in the recovery process is rather heavy as indicated by accumulation factors (32) : potassium 11.6 , chlorides 3.7 .

The accumulation factor is the concentration in white liquor (kg/a.d. ton of pulp) divided by the total amount introduced to the chemical recovery system (kg/a.d. to of pulp). According Wong (231) under similar effluent discharge condition, the progress of potassium accumulation in the liquor system could be at least 10 times faster than for a wood based mill. The equilibrium chloride content in a fluid bed rector system and 90% washing efficiency has been calculated by Copeland (34).

Both potassium and chlorides decreases softening and melting point of B.L. ash. Soda has a melting point of 851 °C which is lowered at 38% NaCl content to 633 °C. No data are available for a Na_2CO_3 - K_2CO_3 system but for a system 66.3% Na_2CO_3, 20.8% Na_2S and 12.9% Na_2Cl the eutectic melting temperature dropped at 5% potassium replacement to 525°C from 590°C. Influence of both chlorides and potassium on melting and softening point of carbonate is demonstrated in the following table :

Table 12

SODA BASE PULPING LIQUOR ASH (TYPICAL) TRACE CONTAMINANT MELTING POINT SUMMARY			
% Cl	% K	Softening point °C	Melting point °C
0.55	0.20	620	780
0.65	0.20	600	780
1.50	0.20	580	780
0.15	0.50	780	810
0.25	0.80	700	780
0.55	1.70	560	770
0.65	2.00	560	770
1.50	2.00	560	780
1.50	3.00	500	770
0.45	1.40	500	740

Source(34)

This depression of softening is dangerous in fluid bed incineration due to lumps building through extensive sticking of soda particles. If the incineration temperature is lowered the residual unburned carbon is too high. There are attempts to counteract this by additive binding chlorides, e.g. CaO (34) or other chemicals (35).

In high temperature incineration depression of melting point of the smelt poses no problem, as the melting point of soda is higher that of soda and sodium sulphate mixture in sulphate pulping. However, due to the higher temperature of the soda B.L. smelt more NaCl and KCl are in the fly ash due to higher vapour pressure of these compounds (20). This is confirmed by long term observations of NaCl content in dust. It is useful to express concentration of Cl and K by fraction Cl/(Na+K) as mole percent (36).

Softening of fly ash by increased potassium and chlorine content results in plugging of boiler tubes. Therefore it is recommended to decrease temperature of flue gases while incinerating straw B.L. to 540°C by water screens.

The softening (sintering) and melting point temperature can be observed by the cone softening method of Reeve (37). Black liquor ash is powdered in a mortar with pestle and the powder is formed in a cone with water as binder, heated in a furnace and observed. Four points are determined -

- first melting (sweating of surface)
- first deformation (cone bends)
- radical deformation
- complete melting.

It was observed, that the first melting point is important in assessment of boiler superheater corrosion, as molten phase accelerates corrosion. It has been shown, that the deposit first melting point is lowered by potassium only. The mole fraction of K and Cl is important for melting and corrosion and it is useful to reduce superheater temperature in relation to K mole percent. This is obviously very important for straw B.L. firing, as straw B.L. potassium content is high.

It should be noted, that chlorides can be removed from fly ash by dissolving fly ash, saturating with CO_2 to form sodium bicarbonate, which is much less soluble, than sodium chloride (36).

3.2 Silica in the chemical recovery system

3.2.1 Sources and reactions of silica

Silicon in the form of silica (SiO_2) and silicates is the most important non-process-element (NPE). The sources of silica in the recovery system are the fibrous raw material, the limestone, water and in case of kraft pulping the make-up salt cake (32). According Panda (6b) in bamboo pulping about 70-80 % of silica is from bamboo, about 5 % from salt cake and about 20 % from lime. In the cooking process the silica contained in the fibrous raw material is partly or nearly completely dissolved (see section 2.2) in the sodium hydroxide forming sodium silicate (Na_2SiO_3). This is a salt of a strong base (NaOH) and weak acid (silicic acid). It hydrolyses in water solution to sodium hydroxide and silica :

$$Na_2SiO_3 + H_2O \rightleftharpoons NaOH + H_2O + SiO_2$$

The equilibrium is dependent on residual alkali in the black liquor and consequently on pH. Amorphous silica is on the other hand in equilibrium with monosilicic acid, $Si(OH)_4$. Higher RAA will shift the equilibrium to sodium silicate, which is very soluble in water. Lowering RAA and pH will result in formation of less soluble silica and silicic acid. Solubility of amorphous silica at various pH is shown in Table 13.

Table 13

SOLUBILITY OF AMORPHOUS SILICA						
pH of solution	1	4	6	7.7	10.3	10.6
SiO_2 solubility at 25°C, %	0.014	0.013	0.011	0.010	0.049	0.112

Source(13)

Reducing RAA and lowering pH results in precipitation of silica causing various problems in the recovery system.

Solubility of silica is temperature dependent. Kulkarni (38) determined solubility of precipitated silica after reducing pH of black liquor to 10.4 with CO_2 at 17°C. The carbonated liquor was heated to various temperature and silica content in supernatant liquor after centrifuging was estimated (Table 14).

Table 14

EFFECT OF TEMPERATURE ON SOLUBILITY OF PRECIPITATED SILICA

Temperature °C	17	38	45	55	70
SiO_2 g / l	0.40	1.96	2.10	2.40	3.00

Source(38)

To prevent precipitation of silica from the black liquor in various phases of the recovery process sufficient RAA should be maintained to keep pH at the desired level. The black liquor is a complicated system containing buffering compounds such as sodium salts of organic acids. The residual alkali is consumed during storing of black liquor resulting in sludge formation. Local decrease of pH e.g. caused by suction of CO_2 containing air through the wire mesh of the washing filters may also result in silica precipitation.

Sodium silicate reacts with calcium and aluminium ions resulting in insoluble compounds. The most important reaction is with $Ca(OH)_2$ in green liquor causticizing is

$$Na_2SiO_3 + Ca(OH)_2 \rightleftharpoons CaSiO_3 + 2NaOH$$

The reaction is not quantitative. The equilibrium probably depending on temperature and NaOH concentration. Some authors (6b) published data, that 30 % of the silica entering the causticizing reaction does not react with $Ca(OH)_2$. Other authors estimated (39, 40) only 7.5-10 % unreacted sodium silicate.

3.2.2 Difficulties caused by silica

The difficulties caused by silica in the recovery system are listed as follows :

- Pulp washing : Colloidal silica particles are plugging the screens (wire meshes) of the washers and are partly responsible for low capacity of washing equipment and low efficiency of washing especially in wheat and rice straw pulping.
- Evaporation : Silica is causing heavy scaling of evaporator heating surfaces especially at concentration of black liquor over 45 %. The chemical composition of evaporator scales from a bamboo (40) and a wheat straw mill (7) are presented in Table 15.

Table 15

ANALYSIS OF MULTIPLE EVAPORATOR SCALE				
	Ash %	**SiO_2 %**	**CaO %**	**Mixed oxides %**
Bamboo pulp mill	84.5	53.8	12.6	17.0
Wheat straw pulp mill (with 20 % reed)	84.97	58.5	11.1	2.6
Expressed as % w/w of scale				

Source(7, 40)

- Incineration of black liquor : "Honeycomb" stickings of silicate are formed on the boiler walls especially when wall drying system is employed. Sodium silicate increases melting point of the smelt thus increasing heat looses with smelt and increasing tendency to black-out of incineration. Deposits on boiler, superheater tubes, air heater and economizer tubes lower heat efficiency.
- Causticizing : Calcium silicate is formed from sodium silicate which impairs sedimentation and washing of lime mud. Soda losses are increased.
- Lime reburning : Slicky rings of glassy silicates are formed. Calcium bound on silica is a loss in lime reburning increasing limestone demand. Depending on silica content a part of the lime has to be purged and fuel consumption is higher. At high silica content no lime reburning is possible.

Evidently the most problems in the alkali cycle are caused by silica deposits. According Panda (41) 22-30 % of total deposits are furnace wall deposits, 22-26 % boiler and superheater deposits, 8-9 % air heater and economizer tubes deposits and 43-45 % evaporator tubes deposits.

3.2.3 Silica outlets

- Some of the silica is leaving the system with the pulp. The silica content in the pulp depends on pulping conditions (see section 2.2) and washing of pulp. In case of bamboo pulp about 10 % of silica originally contained in bamboo are retained in the pulp. This is higher in pulping of wheat and especially rice straw. In case of low residual alkali at the end of cooking silica dissolved in the cooking liquor is redeposited on fibres.

- Losses of black liquor are also an outlet, but does not change silica proportion to alkali.

- Sludge in black liquors tanks may be an important outlet when longer storing black liquor prior to evaporation.

- Scales and deposits in evaporation and recovery boiler have a negative impact on these processes but the percentage of total silica removed is comparatively low.

- Grits from green liquor also contain some silica, but under normal conditions this outlet is low.

- The most important outlet of the alkali cycle is the calcium silicate formed from sodium silicate in the causticizing process. This outlet is actually an input into the lime cycle. In case there is no lime mud reburning this does not effect the recovery cycle. However in case of lime reburning a part of the lime mud has to be purged to keep silica content in lime at an acceptable level (see chapter : Causticizing and lime reburning).

4. EVALUATION OF ESTABLISHED SMALL AND MEDIUM SCALE RECOVERY PROCESSES

4.1 Introduction

This evaluation is based on visits of the author of 6 small and medium size pulp mills with chemical recovery using non-wood raw materials (2 mills in China, 2 mills in India, 1 mill in Brazil, 1 mill in Hungary). Data were also collected from 10 Chinese mills sending to these mills a detailed questionnaire. All questionnaires are included in a UNIDO report (10). Further data were obtained by correspondence with mills, machinery suppliers and experts, by evaluating UNIDO reports and publications in technical journals. In this chapter equipment operated in industrial scale or at least tested for non-wood pulp is discussed.

Every sub-process and operation is evaluated by estimating differences when compared with standard processing of wood pulp and wood black liquor in large size mills (more than 200 TPD). Whenever possible differences are identified to be caused by :

- small scale operation
- processing of non-wood fibrous raw materials.

Influence of scaling down standard equipment is discussed. In this report the chemical recovery is characterized as follows :

Overall chemical recovery efficiency is the percentage of total alkali recovered in the white liquor related to total alkali in the black liquor after cooking

Overall thermal efficiency is the heat value of steam generated in the recovery boiler from black liquor solids (without heat from auxiliary fuel) minus heat in steam used for evaporation of black liquor.

The efficiency of individual sub-processes is specified in the respective chapter/section.

4.2 Unbleached pulp washing

4.2.1 General description

The washing process is a pre-stage of the recovery system and has an important influence on the economy of the recovery system. The washing efficiency determines to a large extent the overall chemical recovery and the concentration of the black liquor the overall thermal efficiency of the system.

In small and medium size non-wood mill the same equipment is used as in standard wood pulp mils i.e. :

- vacuum drum washers
- pressure drum washers (Rauma - Repola)
- displacement presses (Sunds - Defibrator)
- belt washers

The physical processes are :

- leaching of soluble substances from the fibres by diffusion in diluted fibre suspension and draining-off the solution (diffusion washing)
- displacement of the black liquor from the capillary system of the pulp mat by wash water/liquid characterized by displacement ratio (DR). Actually more water is used to displace the liquid in the pulp mat than the volume of water in the pulp mat and the excess water is diluting the black liquor. This dilution is specified as dilution factor (DF) in tonnes of water / t of pulp. The better the displacement the less water has to be used in washing and the higher is the washing efficiency.

The higher is the DF the better the washing efficiency, but the lower the black liquor concentration. The dilution factor in wood pulp washing on drum filters is usually 2.5 to 3, on belt washers around 1.

Temperature of the washing water should be 70 - 80 °C as every 10 °C increase of temperature doubles the rate of diffusion of soluble substances from the fibres into the wash water between the fibres.

Specific properties of non-wood fibres especially of straw pulps have a negative impact on the pulp washing process :

- Drainage of the pulp slurry is slow as fibres are short, specific surface of the fibres is high. Consequently, freeness of the slurry is low (high °SR).
- Precipitated or colloidal silica plugs the openings of the wire mesh of the washing equipment (drums, wire of the belt washers). This reduces capacity and drainage rate.
- The short fibres having a large specific surface form a more dense fibre mat. The density of the rice straw pulp mat is by 50 % higher than of bamboo pulp mat. The pulp mat is difficult to penetrate, displacement washing is less effective, washing efficiency is lower.

Scaling down standard washing equipment (drum washers, belt washers) does not cause mechanical problems, but at lower width of pulp mat the so called "edge effect" has a larger influence. The edges are either less washed, or the wash water overflows the edge diluting B.L. No quantitative assessment of this effect is available.

4.2.2 Drum washers

Vacuum drum washers are mostly used in non-wood pulp washing as 3-stage or 4-stage countercurrent washing. Drum washers are manufactured by several companies in China and India (see Annex II.). The loading capacity of drum washers is considerably lower for non-wood pulp, but data from different suppliers and different mills are in a wide range (see Table 16).

Table 16

LOADING CAPACITY OF DRUM WASHERS t/m²/d						
	Wood	Bamboo	Reed	Bagasse	Wheat straw	Rice straw
Mill data	5-8	3-4	3.8-4.5	3-4.5	1.6-1.8 x	-
Suppliers data	5-8	3-4	up to 5	2-3	1.55-2	1.28 xx

Source(10)

x - with 30 % rice straw xx - only one supplier

Suppliers data and mill data differ in some cases as the washers in mills are frequently overloaded but sometimes underloaded. The operation of drum washers is smooth with bagasse pulp, but difficult with straw pulp. The wash water is flowing back on the surface of the drum to the washer vat as penetration of washing liquid is difficult.

Dilution factors claimed by the mills are in a wide range (2-4.3), but data are not reliable as no exact measuring of flow rates is available in visited mills.

In a few cases Rauma-Repola pressure drum washers are used. This type of washer has 3 stages on one drum. The washing liquid is not sucked by vacuum but pressed through the fibre mat by air pressure. The loading capacity in the Hungarian wheat straw pulp mill is about 2 t/m²/day. It is used in combination with displacement presses.

4.2.3 Horizontal flat washers

Horizontal flat washers are a comparatively new development derived from Fourdrinier paper machines. The pulp from the headbox is transported by the fabric wire to the discharge end. Several vacuum suction boxes collect the liquid. The pulp mat passes under showers where the filtrate from the succeeding washing stage flows onto the mat. The dilution factor in wood pulp washing is approx. 1, but washing efficiency on wood pulp on one machine is high (98-99 %). The horizontal washers were successfully installed in many wood pulp mills.

In China horizontal 5-stage horizontal washers have been developed by two companies (see Annex II.) and installed for non-wood pulp washing. Initial information was quite optimistic (21) but data obtained from Chinese mills and by visiting a mill are less encouraging. Dilution factor is 2 to 3 and washing efficiency 80-85 % only. The inlet consistency is 3-4 % outlet consistency claimed by suppliers should be 15-19 %. However mill data show outlet consistency 12 % only (see Annex III. - Xin-Hua Mill Shanghai). The actual loading capacity is up to 1.6 t/m^2/day. The Delcor horizontal washer is successfully operated in a South African bagasse mill, but no data are available. Delcor horizontal washers will be manufactured also in India (see Annex II.).

The Naco flat washer is inclined to reduce the tendency of the washing water to follow the pulp mat due to its poor drainability. The angle could be adjusted according drainability of the pulp. The washing table is equipped with foil boxes. The first section has a short barometric leg, the second is connected to a low vacuum by a fan and the last to a vacuum pump (higher vacuum). The washer is equipped with a 50 mesh SS wire to reduce fines in filtrate. The prototype was tested in mill conditions in the Foggia wheat straw pulp mill (Italy).The washing efficiency at various dilution factors is shown in Table 17. The washing efficiency is higher than in the Xin-Hua Mill, but that is using 30 % rice straw.

Table 17

WASHING EFFICIENCY OF NACO FLAT WASHER (ONE STAGE)

Pulp mat consistency %	Dilution factor (DF)						
	0	1	2	3	4	5	6
10	78.95	83.03	86.32	88.96	91.06	92.74	94.08
14	78.95	84.05	87.96	90.90	93.09	94.73	95.95

The Andritz Double Wire Washer consists of two converging wires forming a wedge section where the pulp slurry is dewatered by gravity and wire tension to 15-17 % dryness. The wedge section is followed by a washing module with 3 washing shoes. Pressure water is entering the 3rd compartment and the drained liquid is pumped as washing liquid countercurrently into the 2nd and first compartment. The pulp mat after the washing section can be pressed to 25-40 % dryness in 3 press nips. This type of washer was successfully applied to wood pulp, but no industrial applications are known for washing unbleached non-wood pulps. CPPRI (India) tested in a UNIDO project a pilot double wire washer in short time experiments for washing of bagasse, rice and wheat straw pulp (5). When using one washer a washing efficiency at DF 3 a washing efficiency about 87 % could be achieved for straw pulp and about 91 % for bagasse pulp without considering pressing of pulp, as it is difficult to use the pressed-out liquid. Computer simulation has shown, that by combining two double wire washers a washing efficiency of 92-93 % could be achieved. A similar horizontal washer is the Belmer type.

4.2.4 Wash presses

The Sunds Defibrator's Displacement Press consists primarily of two synchronous, counter-rotating dewatering rolls in a pressurized vat. The vat has dual pulp inlets. A pulp sheet is formed in the dewatering zone between the rolls and the tapered baffles. At the end of the baffles, pulp consistency is approximately 10 % and washing liquor is added into the displacement zone.

The procedure with dewatering the pulp on perforated rolls, followed by the addition of fresh washing liquor in the displacement zone, results in efficient washing. This is increased when the pulp is pressed in the roll nip to a discharge consistency of up to 35 %. The pulp leaving the nip is discharged into a shredder conveyor mounted above the rolls. Filtrate leaves through the openings at the ends of the rolls and is discharged through two outlets in the bottom of the vat.

Sunds-Defibrator presses are used in the Hungarian wheat straw pulp mill after a Rauma-Repola pressure drum washer (see Annex III.). The estimated washing efficiency is about 90 %, but no exact data are available. A similar combination is being installed in the Chinese Xin-Hua mill. The Italian Foggia wheat straw pulp mill has also a Sunds press. Suspended solids content in weak black liquor are very high (in Hungary up 5,000 mg/l, in Foggia up to 10,000 mg/l).

4.2.5 Total dissolved solids in weak black liquor

The TDS concentration in weak B.L. from agricultural residues and grasses is low, 7-9 % only, in some cases (bagasse) up to 10-11 % in contrary to wood and bamboo weak B.L. (14-16 %). This is the result of following reasons :

- pulping is with direct steam-condensate dilutes B.L.
- dilution factor is higher, than in wood pulp washing
- normally black liquor is not recycled in agricultural residues pulping.

It is claimed, that this is not possible due to high suspended solids (fines) content in B.L. which will reduce drainage rate and permeability of pulp mat. Another reason is a too high content of non-degraded hemicelluloses in B.L. which reportedly would result in substantial increase of alkali consumption (42).

Low B.L. concentration increase steam consumption in evaporation by 50-60 % when compared with evaporation of wood B.L. to same concentration.

4.2.6 Separation of suspended solids from B.L.

Suspended solids (fines) content should be in the range 5-25 mg/l, but certainly under 50 mg/l. Short fibres (fines) may increase fouling of evaporators. The suspended solids content in agricultural residues B.L. is very high (1,000 - 5,000 mg/l). Most of the mills use vibrating screen with 100 mesh wire, but filtration is not sufficient, SS content may be 150 mg/l. Dorr-Oliver DSM screens are also used. A South American bagasse mill uses Maloney drum filters with 100 mesh SS filter cloth. The Hungarian mill has a filter of own design.

4.2.7 Conclusion

Washing of unbleached pulp from agricultural residues and grasses in small pulp mills especially from wheat and rice straw is a weak point of the recovery system for following reasons :

- Loading capacity of drum and horizontal washers is considerably lower than for wood pulp
- Washing of these pulps requires a high dilution factor (DF 3-4)
- Washing efficiency is generally between 85-90 %, for bagasse up to 95 %.
- Dry solids concentration of weak black liquor is low mainly as a result of low concentration of the black liquor entering the washing line from the digester and also due to the high dilution factor. The concentration is generally 7-9 %, but with bagasse can be up to 10-10.5 %
- Suspended solids (fibre fines) content is high (with straw pulps up to 5,000 mg/l)
- Operation of the washing line is poor, imperfect distribution of washing liquid, no monitoring of the process.

4.2.8 Recommendations for development

- Installation of flow measuring or preferably control instruments (if possible including flow of pulp).
- Implementation of a pulp washing monitoring system preferably in a framework of a UNIDO project. Monitoring methods should be standardized, evaluated by UNIDO experts and the washing process optimized.
- Evaluation of further development of horizontal washers, testing of gradual increase of vacuum on pulp mat density and permeability to washing liquor.
- Detailed evaluation of black liquor filtering equipment including precoat filters.

4.3 Evaporation and concentration of black liquor

4.3.1 Introduction

The weak black liquor from the washing of pulp has a concentration of solids usually 14 to 17 % in wood pulping and 7 to 10 % in agricultural residues and grasses pulping. The wood weak black liquor in older installations is evaporated to 50 % or more in multiple effect evaporators with indirect steam heating and to 62-65 % in direct contact evaporators. In modern installation the wood black liquor is concentrated in concentrator-evaporators to 63-65 % and in most modern mills to 70-75 %. In small agro - based pulp mills with recovery the weak black liquor is evaporated usually to 43-45 % only and in direct contact evaporators to 52-60 % concentrations of soluble solids.

Evaporation of black liquor is an energy consuming operation. The evaporated volume of water is much higher with agricultural residues black liquor when compared with wood black liquor. Approximative water volumes to be evaporated to various solids concentration for wood and agricultural residues black liquors are presented in Table 18.

Table 18

APPROXIMATIVE VOLUME OF EVAPORATED BLACK LIQUOR TO VARIOUS B.L. CONCENTRATIONS

Type of B.L.	Concentration of weak B.L.	Evaporated water t/t of unbleached pulp		
		45 %	50 %	65 %
wood	14 - 17 %	6.3- 5.6	6.57- 5.93	6.64- 6.17
agricultural residues (wheat straw, bagasse, reed)	7 - 10 %	13.9-10.0	14.2 -10.36	14.8 -10.95

The differences are given for a certain type of pulp by yield, chemical charge and washing losses. The high weak B.L. concentration and consequently low evaporated water amount in case of wood pulp is a result of good washing efficiency (96-98 %), low dilution factor and mainly by weak black liquor recycling to the cooking process. This is normally absent in case of agricultural residues pulping.

4.3.2 Basic principles of evaporation

Evaporation is a heat transfer operation.

Heat transfer : Heat transfer in an evaporator is governed by the following equation :

$$Q_T = U.A.\Delta T$$

where Q_T = Heat transfer rate
U = Overall heat transfer coefficient
A = Surface area
ΔT = Temperature difference between heating vapour and liquor

The components of the overall heat transfer coefficient have the following relationship :

$$U = 1 / \sum r$$

where $\sum r$ = Thermal resistance

$$r = r_{dt} + r_{ds} + r_m + r_{ft} + r_{fs}$$

where r_{dt} = fouling resistance (tube side)
r_{ds} = fouling resistance (shell side)
r_m = metal resistance
r_{ft} = film resistance (tube side)
r_{fs} = film resistance (shell side)

The above relationships for tubular evaporators also apply to evaporators which use plates.

Scaling : Scaling or fouling is the most significant operating problem with evaporators. The most obvious indication of scaling is an increase in ΔT, i.e., live steam temperature (and pressure) will tend to rise. Excessive scaling of the evaporators will require a shutdown and washing.

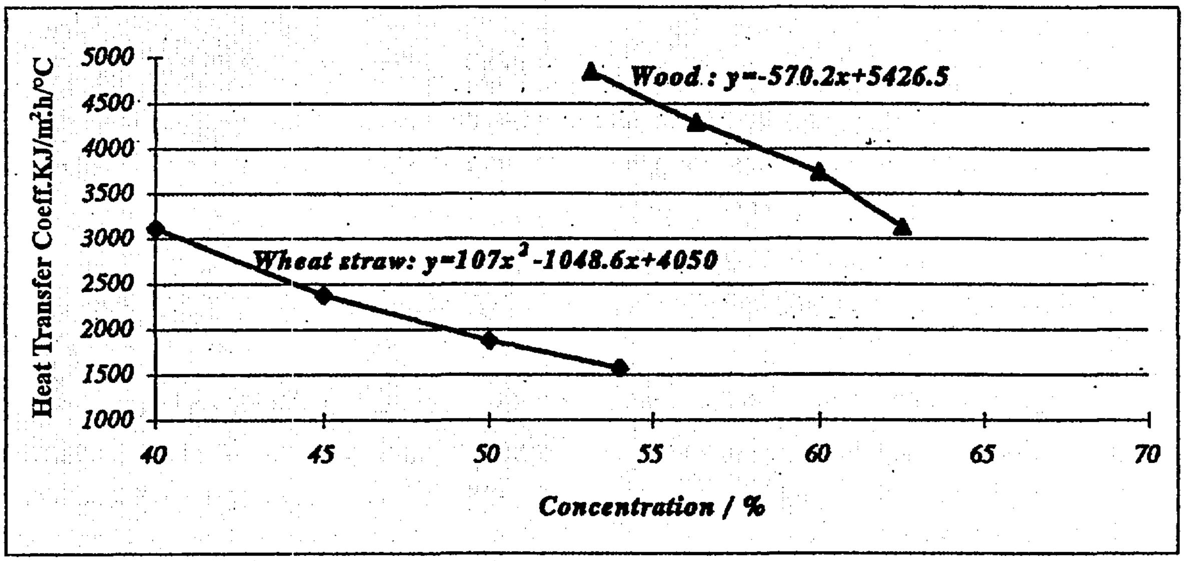
Two types of scale predominate in wood B.L. : Calcium carbonate, sodium sulphate-sodium carbonate (Burkeite). Burkeite scales are water-soluble whereas calcium carbonate scales are not.

In agricultural residues black liquor silica is the predominate scale (see chapter 3). To keep silica as far as possible in solution sufficient residual alkali is required. Desilication will reduce fouling resistance (tube side).

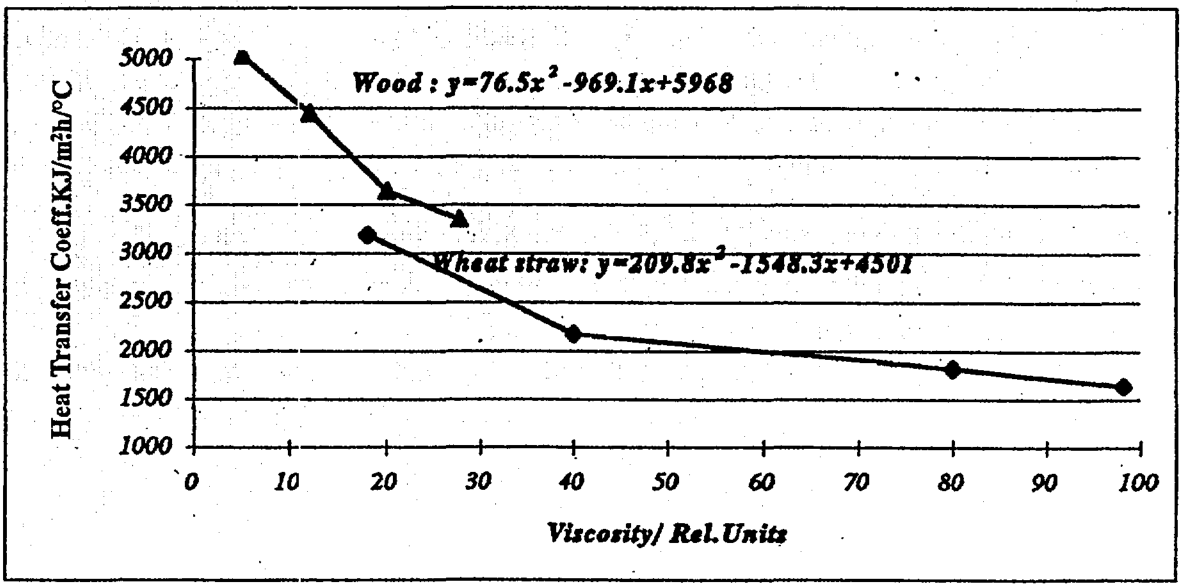
The film resistance (tube side) will increase with increasing viscosity. As viscosity is increasing with soluble solids concentration of the black liquor, consequently, with increasing concentration the film resistance increases. The influence of black liquor concentration and viscosity on heat transfer rate has been investigated by Chinese authors (23f) on an experimental falling film plate evaporator using wood and wheat straw black liquor. The inlet concentration of black liquor was over 40 % (Fig. 5). At same black liquor concentration soda wheat black liquor shows about three times lower heat transfer rate when compared with wood kraft (sulphate) black liquor. The heat transfer rate of wheat black liquor was at same viscosity only slightly lower than that of wood black liquor. This difference may be a result of higher scaling with wheat straw black liquor even after a short time during this experiment.

While scaling is time dependent and, consequently, the thermal resistance due to scaling is increasing with time, viscosity is constant in a certain evaporator body and consequently this part of the thermal resistance is constant. Consequently, evaporator bodies with higher B.L. concentration will evaporate less water per unit heating surface area. Viscosity of B.L. can be reduced by sufficient alkali content in black liquor. This should be 6-8 g/l or more. The film resistance can be also reduced by increasing flow speed. Fibres are attached on rough surfaces, i.e. where primary scaling is already present. It is necessary to reduce fibre content in black liquor by filtration.

Influence of Black Liquor Concentration on Heat Transfer Coefficient



Influence of Black Liquor Viscosity on Heat Transfer Coefficient



Note: Based on data of Tianjin Institute (China) (23f)

Fig. 5

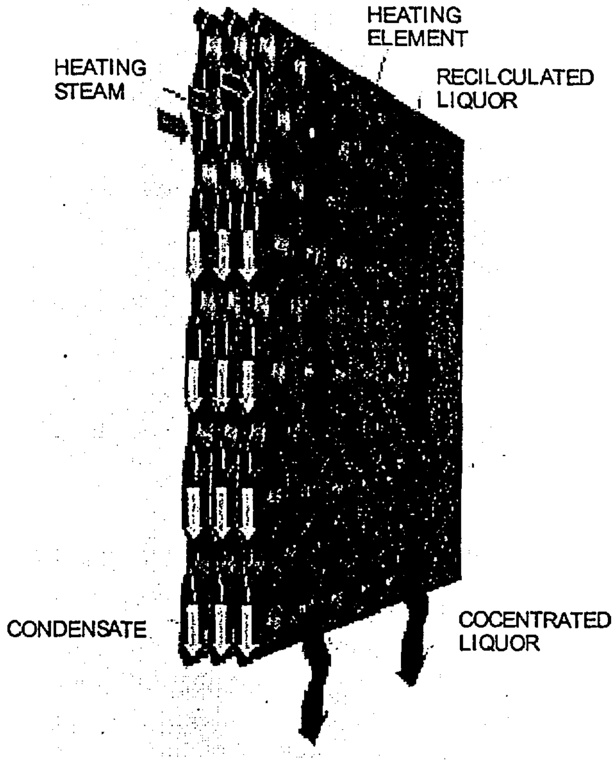


Fig.7
FALLING FILM EVAPORATOR PLATE
/Wagner - Biro-LO - SCALE/
Source: TMT, India, leaflet

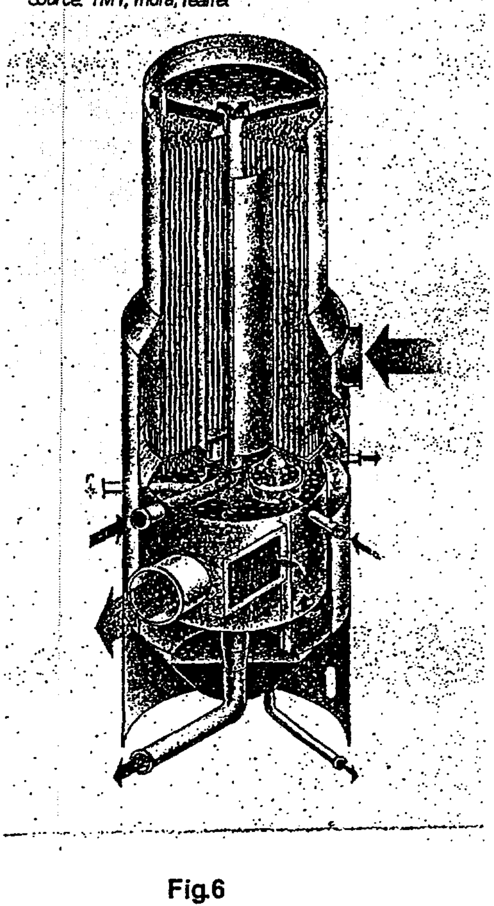


Fig.6
TUBE FALLING FILM EVAPORATOR
Source: Tampella leaflet

4.3.3 Evaporator and concentrator types

In evaporators wood black liquor is evaporated by indirect steam heating to about 50-55 % dry solids concentration. Agro-based black liquors are evaporated to 40-45 % only due to high viscosity and scaling tendency. Concentrators evaporate black liquors to over 50 % dry solids concentration.

The most important evaporator types are :

- Short tube vertical (STV) evaporators using 1-3 m tubes with natural circulation. The B.L. is heated in the tubes, but most of the evaporation is in the vapour head, this reduces scaling in tubes. However, heat transfer in the tubes is low as liquor velocities are low.

- Long tube vertical (LTV) evaporators with natural circulation use 8-9 m long tubes. These are rising film evaporators. The liquor rises under pressure through the tubes and is heated by steam surrounding the tubes. With liquor rising the static head of the liquor decreases and at some point of the tube the liquor starts to boil. The liquor-steam mixture is pushed through the boiling section with high velocity. In this section the internal walls of the tube are not always uniformly wetted by new rising film which is a mixture of steam and liquor. This may result in local spot overheating and increased scaling, therefore LTV evaporators for higher concentration scale quickly.

- Long tube vertical (LTV) evaporators / concentrators with forced circulation (FC) are used for concentrating wood black liquor to concentration over 50 %. The tubes are usually shorter (4.2-7.3 m) and of smaller diameter, with high tubular velocities, but the risk of plugging increases. FC crystallizers use external heaters in which is only sensible heating and evaporation occurs when the heated liquor flashes in the associated vapour body. Scaling tendency is less in crystallizers.

The most modern evaporators / concentrators are of falling film type.
The vertical tube Falling Film Evaporator (FF) (or Free Falling Film FFF) consists of a heat exchanger mounted concentrically on top of the vapour head, a circulation pipe and a pump. The vertical tubes of the heat exchanger are rolled into the top and bottom tube plates. In a Falling Film Evaporator the liquor is circulated from the lower liquor sump to the upper liquor chamber, where it flows through the liquor distributor to each tube. The circulation and the distribution are designed to ensure that each tube is continuously wetted with liquor. (Fig. 6)

As the liquor flows down inside the tubes, steam/vapor is condensed on the outside of the tubes, causing the liquor inside to evaporate. A mixture of concentrated black liquor and vapour flows out from the bottom of the tube bundle. The vapour is separated from the liquor in the vapour head below. The liquor is then recirculated back to the top and the vapour passes through mist eliminators.

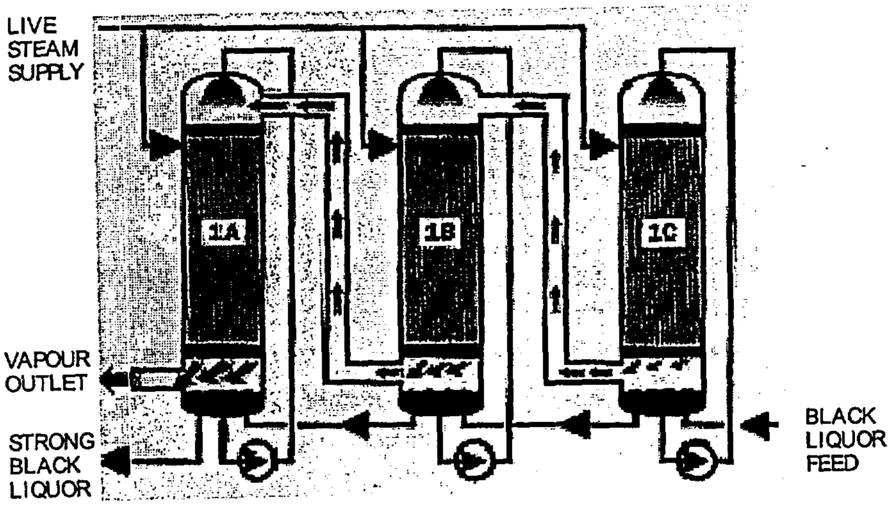
The liquor film falling down the tubes is thin, so it is extremely turbulent, conducting heat from the tube efficiently into itself. Furthermore, evaporated vapour also flows down on the inside of the tubes. The improved heat transfer efficiency allows falling film units to be smaller than rising film units to achieve same evaporation capacity. The effective turbulence of liquor film effectively prevents scaling by making sure the conditions in the film are uniform all over the tube. The liquor distribution system for a tubular falling film unit is efficient, so the amount of circulating liquor can be minimized. The electric power consumption is minimized because the pressure difference over the pump is only equal to the gravitational difference between liquor chambers without any restrictions. Because liquor does not boil in falling film evaporators but evaporates straight from the surface of the liquor film, systems also work efficiently on partial load.

Vertical FF tube evaporators are manufactured by several companies e.g. by Tampella, Lurgi, Goslin-Birningham (43) and also by Epytek (Spain) (see Annex II). In the vertical plate type FF evaporators / concentrators the heating elements are plates of undulated surface (Fig. 7). The heating steam is fed into the inside of the heating elements and removed as condensate and/or non-condensibles at the bottom. The liquor is pumped to a distribution tray on top and flows downwards along the outside of the heating elements. The boiled-off vapours are released laterally into the evaporator body and leave the evaporator via mist eliminators. The liquor not being boiled off is collected at the bottom of the evaporator vessel and is delivered again to the distribution tray together with the feed liquor by recirculating pumps. A partial flow leaves the evaporator as product.

The surface evaporation taking place directly at the heating surface has the effect that the plant can be operated with much less recirculating quantities. From that, on the one hand, an essentially lower residence time of the product is derived and, on the other, an advantage from the energetic point of view: the recirculation pump requires much less energy. Due to several factors, falling film evaporators yield better heat transfer rates under comparable operating conditions than forced circulation rising film evaporators. The undulated surface of the heating elements increases the turbulence and thus the heat transfer.

It is claimed by manufactures that the formation of scale is reduced by self-cleaning of the corrugated surface (split-of of scales).

FF plate evaporators are manufactured by Ahlstrom (Finland), Wagner-Biro (Austria) and in license in India by Pas Construction, Enmas and TMT (see Annex II), but no installation is known so far by these companies for straw and bagasse. Chinese companies developed own design. These FF plate evaporators are installed in some non-wood small pulp mills in China (see Annex II and Annex III) as first effect.



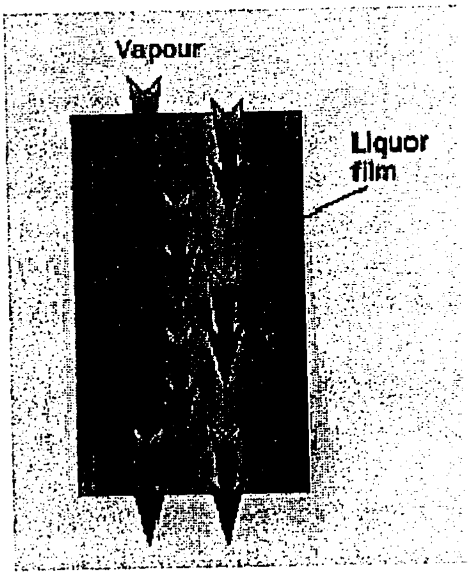


Fig.8
PRINCIPLE OF FF EVAPORATOR
WITH VAPOUR RECYCLING
/Epitek and Kvaerner REVAP/
Source /Kvaerner leaflet/

4.3.4 Concentration and superconcentration of black liquor

In wood pulp mill the black liquor is evaporated to 50-55 % in conventional multiple effect evaporators, usually LTV evaporators. In old mills the black liquor was concentrated to 62-65 % in direct contact evaporators, where hot flue gas from the recovery boiler is brought into direct contact with black liquor. The flue gas cools, and sensible heat given up supplies the latent heat to evaporate water from black liquor. Usually the temperature drop of the flue gas is 140 °C and the B.L. is concentrated from 50 to 65 %. There are two types of direct contact evaporators : the cascade and the cyclone evaporators. These devices are still used in old and new non-wood mills concentrating black liquor from 43-45 % to 52-55 %.

In new wood pulp mills indirect concentrators are used. These are usually falling film evaporators (tube or plate type) concentrating black liquor to 62-65 % concentration and in some cases 67 %. This is at present time not possible with agro-based black liquors as these have a too high viscosity and high scaling tendency.

In wood pulp mills the development is focused on high-dry solids incineration (70-80 % concentration), i.e. superconcentration.

The Tampella superconcentrator is essentially a tube falling film evaporator (see section 4.3.3) working under pressure at high temperature to overcome difficulties with high viscosity. The B.L. in the FF concentrator is heated with 1.0 - 1.2 MPa steam to 170 °C. The superconcentrated B.L. is entering the recovery at 140 °C. The flash steam from the superconcentrator is used to generate 0.4 MPa steam or is used in the conventional MEE train. Superconcentration of non-wood B.L. is at present time not possible due to higher viscosity of B.L. and high scaling tendency.

A new development is the Epytek concentrator which also licensed to Kvaerner group. The heat exchanger of this FF concentrator is split in to six sections, called S1A, S2A, (both in only one shell, H1A); S1B, S2B, (id. H1B); and S1C, S2C, (id. H1C): only four sections will be on line, the remainder two on stand-by. The vapour from the previous section is recycled increasing vapour speed (Fig. 8).
A suitable set of ducts, pipes and valves enable the system to work as follows :

- S_{1A} - S_{2A} - S_{1B} - S_{2B} , the H1C remaining stand-by; or,
- S_{1B} - S_{2B} - S_{1C} - S_{2C} , the H1A being stand-by; or finally,
- S_{1C} - S_{2C} - S_{1A} - S_{2A} , in what case the H1B will be stand-by.

It is clear that depending on the cycle, the black liquor coming from the second effect will be fed into the S1A, or into the S1B or into the S1C, and the corresponding strong liquor will be delivered from the S2B, or from the S2C or from the S2A.

The three bodies, H_{1A}, H_{1B} and H_{1C} , each one holding two sections, can be switched automatically or manually, as wished.

Generally, evaporated particles on the tube surface have a higher solid content than the film part inside of the tube. The solubility of some inorganic compounds can be surpassed and scaling occurs. It is claimed by Epytek that in this concentrator the liquor/vapour speed is high enough to prevent sticking of particles. This is achieved by increasing the velocity of the other component of the mixture, i.e. the gaseous component, corresponding to the generated vapours of the evaporation. In this concentrator, all heat exchanges sections are fed in parallel with the same live steam. Each section is equipped with a recycling and transfer pump for feeding the liquid in series from section to section and incorporating a device allowing the vapours generated in each section to be fed in series as well as through all the sections.

It is claimed that a combination of :

- the number of sections.
- the number of tubes in each section.
- the diameter and the length of the flush tubes, enables any desired velocity to be obtained.

In addition, the high velocity breaks the liquid into droplets forming a suspension of droplets in a gas, like a mist. The droplets work as a scrapper or hammer for the heat exchange surfaces, stopping the precipitated particles from sticking to the hot walls, therefore offering a scaling-free operation. This mixture of vapour and liquid particles has a much lower viscosity, than the liquid itself. This reportedly makes it possible to reach high solids content in spite of the high viscosity of the concentrated product (superconcentrated black liquor). The concentrator according the manufacturer can deal with liquors having viscosity even higher than 500 cP. The concentrator in pilot scale concentrated wood black liquor to 75 % concentration. This concentrator is successfully in operation in the Smurfit mill in Venezuela for evaporation of high viscosity black liquor from eucalyptus (coloured type). No tests have been carried out with non-wood black liquors. It is proposed for three projects in India for non-wood black liquors.

In the Kvaerner REVAP^{TM} (Epytek licence) (Fig. 8) concentrator released vapour from one of the units in the concentrator is supplied to the subsequent unit in the upper liquor compartment at the top of the evaporator. The vapour then flows through the evaporation tubes together with the liquor, where the vapour shears the falling film to achieve improved heat transfer. The vapour flows in parallel with the black liquor through all the concentrator units. This means that the liquor of the highest concentration is sheared to the greatest extent. Therefore, the greatest improvement of the heat transfer coefficient is achieved where it normally has its lowest value.

Ahlstrom high dry solids technology is based on thermal depolymerisation of black liquor (LHT - Liquor Heat Treatment) resulting in viscosity decrease (29). The semi-concentrated black liquor of 45 % concentration from the second effect is heated by flash steam and medium pressure steam (1.0 MPa) to 175-185 °C and flowing to a pressure reactor. The depolymerized black liquor is gradually flashed (4-5 stages) to atmospheric pressure. The flash steam is preheating the entering black liquor in same number of steps in small flow-through pressure vessels. The depolymerized black liquor can be stored at atmospheric pressure and is pumped to the first effect (a falling film concentrator) where it is concentrated to 75-80 %. There are some installations of this process in Europe for wood black liquor. Kulkarni (30) tested the LHT technology in laboratory scale for viscosity reduction of bagasse black liquor. The viscosity drop is significant and it is presumed, that by this technology bagasse black liquor could be evaporated in falling film evaporators to at least 65 % concentration.

Concentrators are operated in parallel with the multiple effect evaporator (live steam to concentrator and to I.effect) or mostly in series (live steam to concentrator, flash vapour from concentrator to I.effect).

4.3.5 Pre-evaporation of black liquors

Flash steam from continuous and batch digesters can be used for black liquor pre-evaporation. Ahlström company uses a FF evaporator for pre-evaporation. Also vapour recompression evaporators can be used as pre-evaporator. No pre-evaporation of non-wood B.L. has been identified in this survey. Using flash steam may be a good improvement as agricultural residues are cooked with direct steam which results in higher liquor to material ratio at the end of cooking and, consequently, in higher amount of flash steam.

4.3.6 Multiple effect evaporator trains (MEE)

In wood pulp mills MEE evaporate black liquor to a concentration suitable for direct contact evaporators (usually about 55 %) or in combination with a concentrator to firing concentration in a recovery boiler (usually 62-65 %). Only a few wood pulp mills have fluid bed reactors, which incinerate B.L. at 35-45 % concentration The number of effects is usually 5 but in new installations 6 or 7. Most MEE combine rising film LTV evaporators with FC evaporators or in modern installations with FF evaporators. Most modern MEE trains use FF evaporators only .

The steam economy of a standard 5-effect MEE is over 4 t evaporated water per 1 ton of steam. More effects improve steam economy, but investment costs are higher. An economic optimum has to be calculated. The steam flow is I-II-III-IV-V, the liquor flow usually is III-IV-V-II-I. In this arrangement the most concentrated B.L. is heated with live steam. Concentrators are included either in parallel, i.e. heated with live and I. effect also with live steam. This means extra steam for concentration at low steam economy. Modern installations are in series using vapour from concentrator to I. effect or using partly live steam to I. effect and concentrator vapour to II. effect.

The average specific loading in a 5-effect MEE plus concentrator in kg evaporated water per 1m^2/h is 22 kg/m^2/h. The specific loading per effect decreases with increasing B.L. concentration : II. effect about 38 kg/m^2/h, I. effect 18 kg/m^2/h, concentrator 6.5-6.8 kg/m^2/h. This is a result of decreasing heat transfer coefficient with increasing viscosity (43, 23f).

In agro-based pulp mills having recovery boilers the black liquor is evaporated to 40-45 % concentration only due to heavy scaling and very high viscosity at higher concentrations. The black liquor evaporated in MEE is further concentrated usually to 52-53 % concentration in direct contact evaporators (cascade or cyclone type). Most bagasse and straw mills prefer cascade evaporators as these handle better the highly viscous bagasse B.L. However, some mills are using cyclone evaporators.

Four and five effect MEE and in the new mills in India six effect MEE (including a FC concentrator) have been identified in this survey. In some mills forced circulation LTV or FF (plate) evaporators/concentrators are included. Four effect short tube vertical evaporators are used in three Chinese mills, four effect trains using LTV evaporators in two and in one mill LTV forced circulation evaporators. The Hungarian wheat straw pulp mill has a MEE consisting of three STV evaporators and two LTV forced circulation bodies evaporating to 54 % concentration, which is the firing concentration in this mill.

One of the new Indian bagasse mills has a 7 body 6 effect LTV train (No. 1 body is double) plus a forced circulation LVT with outlet concentration 44-45 %, the other mill has a 5 effect LTV rising film plus 2 forced circulation LTV train.

The liquor flow in most installation is III-IV-V-II-I, steam flow I-II-III-IV-V. The liquor flow in the 6 effect MEE is V-VI-IV-III-II-I. The Xin Hua Paper Mill (China) using wheat straw has a 4 effect MEE consisting of STV evaporators with a combined flow. The weak black liquor is evaporated in parallel flow. When its concentration is semi-strong, the black liquor is evaporated in mixed flow until its concentration is strong. In the parallel flow, the weak black liquor is fed to I effect evaporator, as well as III effect evaporator as a supplement in order to keep proper liquor level and circulation quantity in IV effect evaporator. In fact, the parallel flow is the flow in which the weak black liquor is used to clean I and II effect evaporators. The mixed flow consists of two flows. One of which is that the black liquor from a feeding tank is evaporated by III, IV effect evaporators, then is sent to a semi-strong black liquor tank; the other black liquor from the semi - strong tank is evaporated by I and II effect evaporators, then is sent to the strong black liquor tank (23g).

4.3.7 Design parameters and practical experience

The heat transfer coefficient is the basic physical parameter of the evaporation process, which is a heat transmission process. The most important design parameter is the heat flux (43) (kW/m^2). The lowest design heat flux is in the concentrator; this means that U.ΔT is also the lowest compared to other effects. Heat flux is difficult to measure. More convenient is to measure the specific loading of an evaporator train or one effect. The specific loading is the amount of water evaporated per unit of surface area. It is an important parameter in design and operation monitoring.

Since $Q_{Total} = Q_{Evap} \pm Q_{Sens}$
and Q_{Sens} is about 15 % of Q_{Total} so Q_{Total} is approximately equal to Q_{Evap}

Specific loadings (evaporated water) (kg/h.m^2) in individual effects during evaporation of wood black liquor are presented in the following table (43) for a steady-state partly fouled (scaled) operating conditions :

Evaporated water	Concentrator	1	2	3	4	5 effect
Specific loading [kg/h.m^2]	6.9	18	29.5	41	31.5	26.3

As expected the concentrator has the lowest values. The bodies with low concentration had high values but the values for the last two effects were lower than expected. High vapour velocities in the last two effects give high pressure losses in the vapour ducting which reduce the total available ΔT.

The average specific loading coefficient for a five body evaporator with a concentrator for wood black liquor is about 20-25 kg/h/m^2 for wood black liquor. For more bodies the specific loading will be less and the required surface larger as the total available ΔT is reduced by the cumulative boiling point rise (BPR). The total available ΔT for an evaporator train is :

Live steam temperature - (Surface condenser saturation temperature + cumulative boiling point rise + temperature losses due to friction in vapour ducts).

Only average specific loading data are available for non-wood black liquors. According Zon Pei Chang (23g) the average specific loading for evaporation of wheat and rice straw black liquor (70:30) in a 4 effect evaporator train is 10-12 kg/h.m^2. The review of Chinese mills indicated for straw a value of 8 to 10 kg/h.m^2, for reed 14-18 kg/h.m^2. The loading factor for bagasse and bamboo black liquor is generally 15 to 17 kg/h.m^2 including in the two new recoveries in India. Very low values for some bagasse mills in China (8-9 kg/h.m^2) and even for reed are in some low capacity mills (30-50 TPD).

The low specific loading for agricultural residues black liquors is mainly a result of high viscosity of B.L. and high scaling tendency. Another factor may be the low available ΔT. These black liquors are evaporated to about 45 % concentration only and, consequently, the boiling point rise is less than of wood black liquors evaporated to 62-65 % concentration

A useful indicative figure for pre-feasibility studies may be the required evaporator surface per ton of pulp per day to evaporate to 45 % concentration based on the data of surveyed mills :

wheat straw (including 30 % rice straw) B.L.	40-55 m^2/t.day
bagasse B.L.	25-35 m^2/t.day
reed B.L.	22-24 m^2/t.day

These figures are indicative/approximative only and depend on weak black liquor and strong black liquor concentration and specific loading of evaporators. In some cases substantially higher figures were found as the evaporator train was most probably designed for a higher pulping capacity. The indicative figure for wood pulp may be around 13 m^2/t.day. Agro-based pulp mills require at same capacity 2 to 4 times higher evaporator surface when compared with wood pulp production.

4.3.8 Energy consumption

Steam economy expressed as kg evaporated water per kg of steam is an important economic indicator. The evaporated water will depend on number of effects in the evaporator train. The more effects, the more water will be evaporated per unit of steam. For a 5 effect evaporator train in wood black liquor the steam economy is over 4 kg water/kg steam (43). Variations reflect to various configurations. A true five effect set will have the economy of more than 4°. A set with concentrator and first effect receiving live steam will have a lower economy. A set with a stand-by body (one effect always cleaned) will have a better steam economy than a set without a stand-by body which at time of cleaning has one effect less. The theoretical steam economy has to be usually increased by about 5 % due to thermal losses.

The steam economy is according various data published in technical journals / handbooks / reports is dependent on type of liquor as well. For wheat straw black liquor a Hungarian handbook indicates following steam economy (44) :

4 effects	3.3 kg water / kg steam
5 effects	3.7 kg water / kg steam.

Survey of Chinese, Indian and South American (SA) mills (45) indicate following steam economy data (kg evaporated water / kg steam) :

Bagasse (S.A.) 5 effects	3.6 - 3.6 - 3.8
Bagasse (India) 6 effects	4.2
Bagasse (China) 4 effects	2.6 - 2.8 - 3 - 3.2
Bagasse (China) 5 effects	3.0 - 3.2
Wheat straw (China) 4 effects	2.0 - 2.1 - 2.5
Reed (China) 4 effects, 5 effects	2.8 - 3
Bamboo (China) 5 effects	4.1

The South American mills are medium size mills, the Indian mills are new small mills. The Chinese mills are small mills of older origin. It should be stressed, that mill data are usually not exact. The steam economy of evaporation of black liquor with high scaling tendency seems to be lower. A hypothetical explanation may be as follows : Due to scaling the black liquor evaporation is the II - III effect is less than designed due to scaling. Consequently, in the first effect or concentrator more higher temperature live steam has to be used. This reduces steam economy. However, no direct data are

available. The steam economy of a FF (plate) concentrator in parallel in a medium size mill (reed and wood) is 0.64 kg water / kg of steam.
Some evaporator manufacturers in India claim higher steam economy, e.g. :

Bagasse	LTV	5 effects	4.2	straw	4.2
Bagasse	LTV	6 effects	4.8	straw	4.8
Bagasse	FF	5 effects	4.2	straw	4.2
Bagasse	FF	6 effects	5.0	straw	5.0

These data seems to be too optimistic.

In small mills usually low pressure steam only is used (0.12 - 0.6 MPa). In one Indian mill partly medium pressure steam is used (about 12 %).
Electric energy consumption is rather different for natural and forced circulation effects or sets. For natural circulation sets (with max. 1 FC) the electric energy consumption is 2.1-2.3 kWh/ 1 t of evaporated water and about 7.0 kWh/t water for forced circulation when evaporating bagasse or straw black liquor.

Electric energy consumption in pumping of black liquor is much higher for bagasse and straw black liquor and increases enormously with concentration of B.L. as shown in following table :

Table 19

COMPARATIVE PUMPING ENERGY REQUIREMENTS (KW) FOR VARIOUS BLACK LIQUORS

% Total Solids	10	15	25	30	40	50	Increase %
Wood Kraft Liquor							
25 °C	1.0	1.1	1.1	1.1	1.5	1.9	90
80 °C	0.9	1.0	1.0	1.0	1.2	1.3	30
Straw Liquor							
25 °C	1.3	1.4	1.9	6.0	17.6	35.2	3,420
80 °C	1.2	1.2	1.6	1.9	2.9	23.8	2,280
Bagasse Liquor							
25 °C	1.5	1.6	1.7	2.2	10.6	60.5	4,220
80 °C	1.4	1.5	1.6	1.6	2.3	7.4	428

Source (34)

Basis :		
	100 m	horizontal run
	50 mm	nominal pipe diameter
	15 m^3/hr	flow rate
	60 %	pump efficiency
	0 m	static head

4.3.9 Conclusions

Non-wood and especially agro-based black liquors are difficult to evaporate in order of difficulty reed - bagasse - wheat straw. The specific loading is low especially for wheat straw. Steam economy is also lower. There is no experience with rice straw black liquor exempt in mixture with 70 % wheat straw. Scalings has to be removed by frequent washing with condensate/water, alkali, hydrochloric acid or hydrofluoric acid (once a year). Some mills use high pressure water cleaning (23g).

High viscosity is at present time a limiting factor in indirect heating evaporation. The limit is in most cases about 45 %, only in some mill the straw or bagasse black liquor is evaporated to higher concentration. The black liquor is further evaporated to firing concentration (usually 52-53 %, bagasse black liquor in some cases 60-62 %) in direct contact evaporators.

Falling film evaporators (tubular and plate type) offer probably a better possibility. A new and promising development are FF concentrators with flash vapour recycling thus increasing several times flow speed and turbulence, which may prevent sticking of scaling substances to heating surface. In this way it may be possible to evaporate to 60-63 % concentration. However, there is no direct experience with bagasse and straw black liquor.

Desilication (see respective chapter) and viscosity reduction by heat treatment may improve evaporation possibility, but this may be too expensive.

4.3.10 Recommendations for development

- Optimization of the evaporation process on existing evaporator trains with the aim to improve steam economy. A suitable evaluation system should be prepared and optimization carried out preferably in the framework of a UNIDO assisted project.
- To support pilot plant or demonstration plant experiments to high solids evaporation using new types of FF evaporators.
- To test in pilot plant condition sulphate B.L. and compare with soda B.L.
- To follow-up pre-evaporation by flash steam from cooking.
- To compare scaling after desilication and without desilication first in laboratory and if possible in pilot plant.

4.4 Incineration (combustion) of concentrated black liquor

4.4.1 Introduction

The objectives of the incineration process is to reduce substantially water pollution to, recover inorganic chemicals in a form suitable for conversion to cooking chemicals and to use the heat of organic matter combustion for heat generation and evaporation of black liquor by direct contact with flue gases.

In the soda process which is frequently used for cooking of agricultural residues the cooking chemical is caustic soda (NaOH) which in the black liquor is bound to lignin and organic acids. In the combustion process the sodium compounds are converted to sodium carbonate (Na_2CO_3) and dissolved to green liquor which is further converted by causticizing with quick lime (CaO) to caustic soda (white liquor). Consequently, incineration can take place in an oxidative atmosphere. The make up chemical to cover chemical losses is sodium carbonate added to green liquor or caustic soda added to white liquor.

In the sulphate process the cooking chemicals are caustic soda and sodium sulphide (Na_2S). In the combustion process sodium sulphide and organically bound sulphide ions are first oxidized to sodium sulphate (Na_2SO_4) and in the same process under slightly reductive condition reduced to sodium sulphide. The make up chemical is normally sodium sulphate added to black liquor and reduced in the combustion process to sodium sulphide. The sodium carbonate in the green liquor is causticized to caustic soda (sodium hydroxide). Some agro-based mills after introducing chemical recovery switched to sulphate (kraft) cooking or are adding sodium sulphite (Na_2SO_3) to the white liquor which is converted to sodium sulphide in the reductive combustion process.

The principal inorganic compounds resulting from the combustion process are sodium carbonate in the soda cooking and sodium carbonate and sodium sulphide in the kraft (sulphate) process. The melting temperature of sodium carbonate is 851 °C. This is reduced by sodium sulphide in the normal range of sulphidity to below 800 °C. The melting point of the inorganic smelt is also reduced by potassium and chlorides. Silica on the other hand increases melting temperature (see chapter 3).

From the point of view of melting of the inorganic compounds the incineration (combustion) process can be divided to :

- Low temperature incineration i.e. incineration under melting and sintering temperature of inorganic compounds recovering the chemical in ash or pellets form.
- High temperature incineration i.e. incineration at temperatures higher than melting point. The chemical are recovered in form of smelt.
- Mixed systems

4.4.2 Early incineration technology and equipment

A very simple incineration equipment was a roaster. The black liquor after concentration, was fed into a rotating cylinder furnace set at a slight angle from the horizontal and lined with refractory. Incineration took place in the cylinder under the melting and sintering temperature of sodium carbonate. The combustion was incomplete and the product, "black ash" contained besides sodium carbonate a considerable quantity of unburned carbon. Auxiliary fuel was required to keep the cylinder furnace in operation. The black ash was leached for sodium carbonate, which was causticized with lime. Chemical losses has been replaced using soda (sodium carbonate) as make up chemical.

As carbon burning and sodium sulphate reduction to sodium sulphide in rotary furnaces was incomplete a crucible shape smelter has been added to the rotary furnace. The black lash from the rotary furnace was falling to the smelter with refractory lining, where it was melted at high temperature. The carbon was burned out almost completely and the reduction of sodium sulphate (Na_2SO_4) to sodium sulphide (Na_2S) improved considerably. The black liquor was evaporated in indirect evaporators and finally on a direct contact disc evaporator using partially the waste heat of incineration, but heat efficiency was very low, CO_2 content in flue gases was 6 to 7 %. The system had no waste heat boiler. Coal as auxiliary fuel could be combusted on an additional fire grate. The life-time of the rotary furnace lining may lasted several years, but of the smelter lining a much shorter time due to high temperature and agresity of smelt. Losses of chemicals in the combustion process were 5 to 15 % indicating a low overall recovery of chemicals. The capacity was about 15 t/day pulp with one smelter crucible and could be doubled by using two smelter crucibles. A somewhat advanced roaster which could incinerate black liquor from 25-30 TPD pulp production is shown on Fig. 1.

Later a waste heat boiler was added to the rotary furnace-smelter complex and the capacity increased to 100-150 t/day pulp. Such recovery furnaces have been widely used before World war II.

4.4.3 Modern recovery boilers

In recovery boiler drying and carbonation of black liquor droplets, final combustion of carbon and volatile carbon compounds, reduction of sodium sulphate as well as steam production is combined in one space stretching the recovery boiler to a high tower-like 55-60 m high construction (Fig. 2). The recovery boiler has water walls constructed as a wall from water tubes, which are connected to the steam generation system. The black liquor of 60-65 % and in most modern boilers 70-75 % concentration is sprayed into the lower part of the combustion chamber by guns. The droplets are first dried, carbonated and finally falling into the hearth containing the melted sodium salts.

In the char bed of the combustion chamber carbon is combusted and sodium sulphate reduced to sulphide. This is an endothermic reaction consuming some heat generated in the recovery boiler. This heat consumption is next to heat required to evaporate water from the black liquor entering the recovery boiler. In incineration of soda pulping black liquors there is no heat loss due to reduction, but the smelt temperature is higher due to higher melting temperature in absence of sodium sulphide and consequently heat losses with smelt are slightly higher.

The combustion zone is normally separated from the superheater and boiler bank by water cooled tubes - screens - to cool down flue gases. The screen is a part of the steam generation circuit. In most recent wood B.L. installations screens are eliminated and replaced by additional furnace height to compensate the flue gas cooling.

The most important design data of recovery boilers have been reviewed by McCann (87). The capacity of recovery boilers reached 2,500-3,000 tonnes dry solids per day and is in average three times higher than in the sixties (500-1,000 t/day). At present time the hearth solids loading is max. 7,200 kg/h.m^2 and the hearth release rate 10.2 to 10.8 GJ/h.m^2 maximum. However, these values were lower at lower capacities (610 kg/h.m^2 and 9.3 GJ/h.m^2). The flue gas temperature entering boiler/generating bank is

620 to 705 °C max. (insignificant Cl and K)
565 to 620 °C max. (significant Cl and K)

The lower temperature in case of significant Cl and K has to prevent fouling of tubes due to decreased sticking temperature caused by K and Cl. These problems are discussed more in detail by several authors (36, 37) and are important for agricultural residues black liquor containing significant amount of potassium (K).

4.4.3 Low capacity recovery boilers

Low capacity recovery boilers (75-250 t dry solids/day) have been a standard equipment manufactured and used in Europe in the fifties. Basic data of J.M.W. recovery boilers manufactured by Tampella (Finland) are presented in Table 20.

Table 20

J.M.W. TYPE RECOVERY BOILERS (AROUND 1960) TECHNICAL DATA

Basic parameters		Fibrous raw materials		
		Softwood	Hardwood (beech)	Wheat straw
Pulp production (air-dry)	t/day	108	92	70
B.L. dry solids per air dry pulp	kg/t	1,520	1,360	1,580
B.L. dry solids	t/h	6.84	5.21	4.60
High heat value	kcal/kg	3,600	3,600	3,000
Steam generated	t/h	24	18	14.6
Steam pressure	bar	45	41	45
Steam temperature	°C	425	425	420
Heating surfaces				
boiler	m^2	1,436	1,186	810
superheater	m^2	405	235	190
Air temperature after heater	°C	120	120	150 *
Primary air	Nm^3/h	23,000	28,000	24,000
Secondary air	Nm^3/h	12,000	28,000	16,000
Flue gases	Nm^3/h	32,000	34,000	36,000
Fuel oil	kg/h			290

Source (46) * with disc (cascade) evaporator

More advanced recovery boilers for bagasse black liquor have been recently supplied by Tampella (Siam Pulp and Paper, Thailand, 225 TDS/day and Ahlström (Edfu pulp mill, Egypt, 156 TDS/day). China started manufacturing recovery boilers in the sixties (21) and recently also India (see Annex II.).

Agricultural residues black liquors are different than wood black liquors :

- The high heat value of B.L. is lower, usually 12.5-13.0 MJ/kg dry solids.
- The black liquors are fired at lower concentrations, usually 52-53 %, only larger bagasse mills in South America are firing B.L. at 60-62 % concentration.

The low capacity recovery boilers evaluated in this survey had lower hearth solids loading (usually 400-650 $kg/h.m^2$). This is most probably a result of small hearth dimensions. The char bed edge is lower and also loading is lower. The edge proportion in a small hearth is larger resulting in lower loading. The hearth heat release rate is also lower due to lower solids loading and lower heat value. The char bed is less porous as SVR of B.L. is low. Higher temperature and different air distribution is recommended.

In China several modifications of water-wall small capacity recovery boilers have been developed and are in operation in bagasse and straw pulp mills. The capacities are usually 40 to 70 t dry solids / day. The salient features of modifications are :

- Increased temperature of B.L. to 105-110 °C
- Oscillating splash guns have been replaced by stationary vortex type guns for suspension drying instead of wall drying of B.L. The B.L. pressure is low (0.1 to 0.15 MPa). The spray gun position was increased to 5.5 to 6.5 m above the floor to alove drying of B.L. droplets. The droplets should not be too small to minimize fly ash.
- Importance is given to combustion air. Secondary air is introduced between the char bed and spray nozzle to support an intensive oxidizing zone. Tertiary air is introduced above the spray gun to supress fly ash upwards movement to boiler bank. The distribution of air is e.g. primary 35 %, secondary 45 %, tertiary 20 %, temperature 150 °C. Air surplus and pressure is low, 60-80 mm water column for primary, 100-120 mm for secondary air.
- Heat intensity of the combustion chamber is lower than in wood B.L. incineration, obviously due to lower heat value of B.L. and lower solids loading.
- The height of the combustion chamber below and above spray gun is increased, e.g. in ZH12 type recovery boiler (40 t/day dry solids, sectional size 2,090 x 2,090 mm) 6,500 mm under spray gun and 5,000 mm above.
- Fly ash from straw B.L. has a lower softening/melting point and has a tendency to be sticky. The temperature of flue gases before entering the boiler tube tank has to be lowered to 540 °C, which requires sufficient height of the water-walls and additional water cooled screens (panels).
- Reinforced soot-blowing is required. The steam boiler heat efficiency is about 60-65 %. The ZH12 boiler is firing 40 t/day dry solids, heat value 12.56 MT/kg and produces 5 t/h steam 1.27 MPa. Auxiliary fuel is required at least in some cases.

In Hungary a conventional Tampella recovery boiler (capacity 9 t/h dry solids) has been modified to suit better for incineration of straw black liquor. The salient features of the modification :

- straw B.L. concentration was increased from 50 % to 54 % by forced circulation LTV bodies;
- to counteract poor combustibility the combustion zone is compressed towards the lower part of furnace;
- distance between primary and secondary air has been decreased;
- temperature of combustion air was increased to 230 °C.

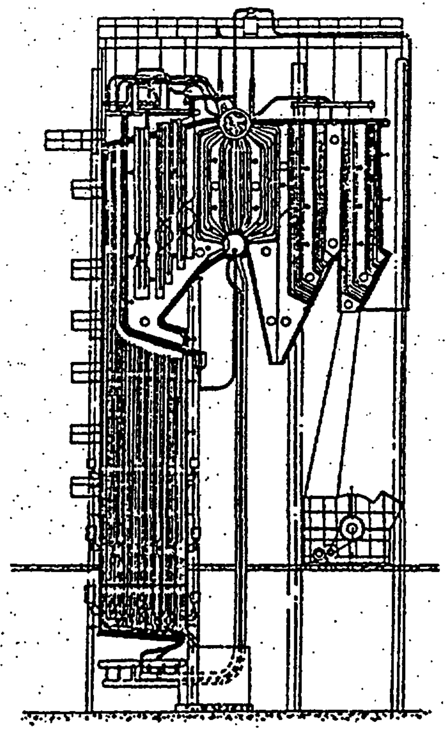
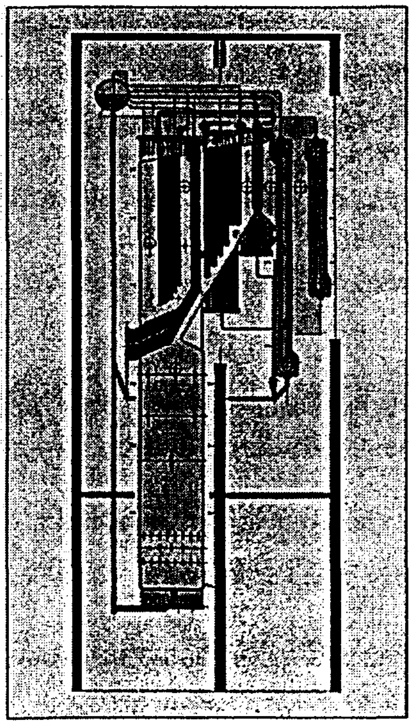


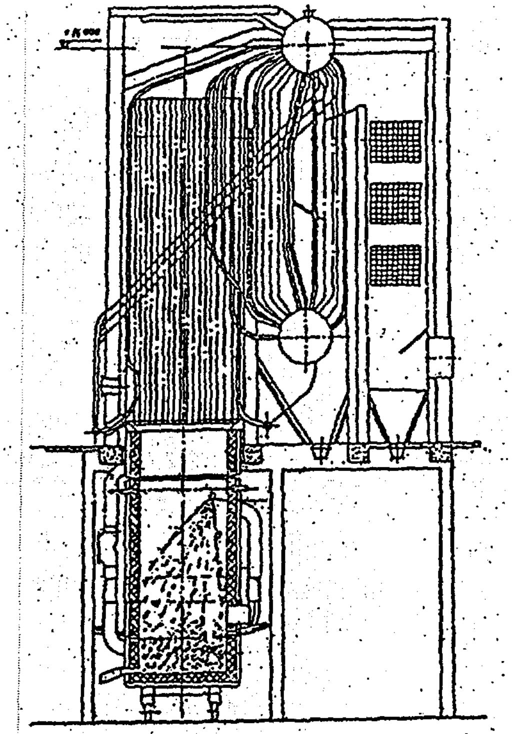
Fig 3. Recovery Boiler In Jilin paper Mill
WGZ-75/39, Wuhan Boiler Works

Fig. 9



TYPICAL ENMAS RECOVERY BOILER
FOR 100% BAGASSE LIQUOR

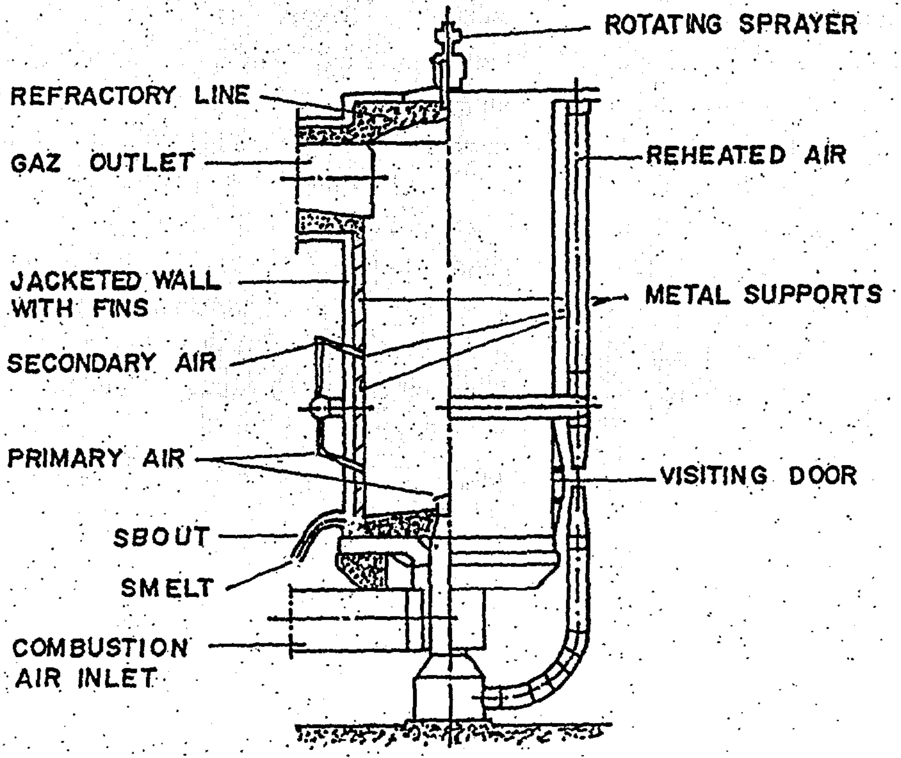
Fig. 10



Semi-waterwall Air-jacket Furnace

Fig. 11

Source /21/



EPYTEK AIR - COOLED REFRACTORY SMELTER

Source /50/

Fig. 12

4.4.4 Salient features of some low capacity recovery boilers

The Xin Hua Paper Mill (Shanghai) is producing 55-60 t/day of unbleached pulp from wheat and rice straw mixture (70:30) (23g). The recovery boiler (in operation since 1989) is a water-wall double drum Wuhan Boiler Work (China) type WGZ-13/Q--1 with natural circulation of water (Fig. 9). The sectional dimensions of the furnace are 2.24 x 2.24 m. The entire boiler is suspended under a top beam of a steel frame. The black liquor at a temperature about 105 °C at 50-52 % concentration is sprayed by three stationary vortex spray nozzles located 7 m above the furnace floor. As B.L. concentration is low and straw B.L. is difficult to dry. The droplets must be smaller than that of wood B.L. The boiler is supplied by primary, secondary and tertiary air (1° and 2° air is preheated from 130 ° to 250 °C in preheaters using flue gas). Primary air ports are at low level. The secondary air ports are placed between the primary air ports and B.L. spray nozzles. Primary and secondary air has a temperature above 220 °C and represents 80 % of total air volume. The tertiary air ports are above the spray nozzles and carry 20 % of total air (pressure 0.1 MPa) ensure complete black ash burning and steamline air flow in the furnace reducing loss of fly ash. The height of the boiler above the spray nozzles is 15 m. Ahead of the boiler bank panel walls are placed to decrease temperature of flue gases to 550 °C or less, i.e. under the fusion (sintering) point of fly ash to prevent hard fouling of convection bank. The panels (screens) are placed vertically so the ash can be cleaned easily by sootblowers or fall down. In order to reduce ash build-up the pitch of screen tubes is enlarged. The boiler has manual and mechanical sootblowing. There is no downtime due to ash build-up. No auxiliary fuel is used. The cooking is actually a low-sulphidity cooking as sodium sulphite (Na_2SO_3) is used as additional cooking and make-up chemical. This has to be ultimately reduced to sodium sulphide, so the combustion is under slightly reductive conditions.

Wuhan Boiler Works WGZ recovery boilers are used in most Chinese small and medium size pulp mills. Out of eleven surveyed mills 8 had Wuhan boilers. Most of the boilers are generating 1.27 MPa (12.7 bar) steam, only three of the surveyed boilers are generating 3.9 MPa (39 bar) steam. Most of the boilers are operated with auxiliary fuel (fuel oil) using various amounts (6-60 kg/t of pulp), the average is around 40 kg fuel oil/t of pulp. Some of the boilers are equipped with electroprecipitators with rated efficiency 98 %.

Several small size mills have recovery boilers ZHP type manufactured by Zhi Gung Machinery Works (see Annex II.). These are water-wall boilers with twin drums. The rated capacity is 25 to 80 t dry solids per day and are designed for bagasse and straw black liquor. The hearth of the ZPH 12 boiler is clad with refractory on water-wall. Detailed description was published by Chen Zhong Xin (23h).

An Enmas (India) recovery water-wall boiler is in operation in the Vindya Mill (see Annex III.) producing at present time 60 TPD bagasse pulp. The Enmas recovery boiler is of Ahlstrom (Finland) design with 3 level air system (150 °C). The boiler (Fig. 10) has wide spaced water cooled screen platens and tangent tube platen superheaters with liberal transverse spacing. This prevents to large extent fly ash deposits. The boiler is of single drum construction with axial flow panel boiler bank. The bagasse black liquor is concentrated in a cascade evaporator to 60-62 % dry solids concentration. The B.L. heat value is about 12.5 MJ/kg (3,000 kcal/kg), temperature about 118 °C. The boiler has two oscillating guns at 5.7 m height. The steam generation is about 2.4 t/t of dry solids, 4.0 MPa (40 bar), 405 °C. The boiler has 10 sootblowers operating 1.5-2 hour per day consuming 4 t steam/h. This is a low percentage of total generated steam (about 240 t/day), but at the time sootblowing causes problems. The boiler has an electroprecipitator with 98 % efficiency. The boiler is successfully operating, but under design capacity due to low capacity of the pulp mill.

An TMT (India) recovery boiler is in operation in the Satpuda bagasse pulp mill (Annex III). The boiler is of water wall (membrane wall) construction. The furnace zone is clad with refractory blocks up to spray gun level (5 m above hearth floor level). The furnace cross section with refractory is 2.3 x 2.1 m, total height 25 m. The unit is designed for 65 t dry solids per day, but at present time operated mostly with 40 t dry solids/day. The boiler has a cyclone evaporator and a Venturi scrubber to reduce fly ash losses. The heat value of the B.L. is 12.5 to 13.3 MJ/kg, firing concentration 54-56 %. The boiler has 4 rotary/retractable sootblowers and 3 air operated sonic sootblowers. These are only sometimes operated as boiler passes are remaining mostly clean. The steam 2.0 MPa generated by the boiler is about 7.5 t/h, steam consumed 2.25 t/h (0.3 LP, 1.95 MP). The boiler operates without auxiliary fuel except of starting.

Even European and American machine manufacturers started to design and manufacture low capacity recovery boilers. Tampella Power (Finland) developed for soda and kraft pulping the Tampella Minor system. Wagner - Biro (Austria) delivered one for incineration of waste liquor from oxygen bleaching, which is actually soda black liquor. The boiler has a capacity 5 t/h dry solids, generating 17 t/h steam 9.5 MPa (95 bar) 350 °C. The boiler is of single-drum construction. Babcock - Wilcox developed the Modular Recovery Boiler (MRB). It is a single drum recovery boiler first installed in a chemimechanical pulp mill in Canada (47, 48). The MRB in this mill can process 223 t/day of dry solids and generate 28 t/h of steam at 4.4 MPa and 400 °C. Babcock - Wilcox is able to supply MRB's rated 135-360 t/day of dry solids, giving steam flows 18-57 t/h.

4.4.5 Air cooled smelters

The combustion of agricultural residues black liquor in low capacity water wall recovery boilers has to be in most cases supported by auxiliary fuel, as the high heat value of black liquor is low and moreover in small furnaces more heat is extracted from the hearth and the combustion process in not sustainable (detailed calculations see in section 4.4.7). A furnace of 2 x 2 m section has 5 times higher hearth wall area, than a furnace of 10 x 10 m section. Air cooled refractory lined furnaces extract in comparison with water wall furnaces only a fraction of heat from the hearth. Air cooled refractory lined smelters have been i.e. developed in China and Spain. The Chinese ZPH 11 recovery boiler has a round, refractory lined smelter, floor area 3.8 m^2 (dia 2.2 m), and 6.1 m^2 (dia 2.8 m) for 40 and 73 t/day dry solids incineration respectively. The smelter is jacketed, air cooled, air outlet temperature 180-200 °C. The smelter is lined with aluminium-magnesium bricks, earlier with chromium-magnesium. The smelter is removable and has to repaired every 3-4-month. A spare one is used. Black liquor concentration is 48-55 %, spray gun height 5.2-5.5 m. The upper part of the recovery boiler is water-walled. The combined smelter-furnace can be operated without auxiliary fuel in spite of very low black liquor concentration (23j).

A very small recovery smelter is in operation in the Mifeng mill producing 25 TPD straw pulp. The black liquor concentrated in a cascade evaporator to 46-48 % concentration has a temperature 90-100 °C and heat value 12.5 MJ/kg.

It is incinerated in a recovery boiler/smelter of total height 16 m. The bottom part is an aircooled jacketed, round, refractory smelter, inside diameter 2 m. The cooling air heated in the jacket is used as primary air. The refractory smelter is on wheels, removable and is combined with a water-walled boiler with electrostatic precipitator (Fig. 11) (21).

The primary objective of the design is to maintain the hearth temperature as high as possible at and above the char bed to sustain continuous combustion. Typical operation conditions are as follows :

Air temperature	primary	250-300 °C
	secondary	180-240 °C
Gas temperature	at boiler bank inlet	500-600 °C
	at ECO exit	260-300 °C
	at EP inlet	140-150 °C
Smelt	temperature	850-870 °C
Electroprecipitator	efficiency	98 %
Steam pressure		0.7 MPa

The hearth heat release rate is just 3.94 GJ/m^2.h which is very low when compared with large wood black liquor boilers (about 10 GJ/m^2.h). In spite of this low heat release rate no auxiliary fuel is required.

The Epytek (Spain) refractory lined smelter has no water-wall boiler connected. Such a smelter is in operation in the Brazil Portela mill for bagasse and bamboo black liquor. The diameter of the smelter is 3 m, height 5 m. The refractory lining is cooled by air which is circulated by a fan through a jacketed wall equipped with fins. This permits the use of only one row of refractory bricks and prolongs the lifetime of bricks (Fig. 12).

The interior metallic ring is provided with metal supports on which the bricks lay. In this way, it is possible to change the bricks by segments, where the parts are most affected by the heat, without having to go through the procedure of lining the entire furnace.

The experience shows that logically the most affected areas are those nearest the air nozzles, because they are the hottest. The average life time of this area can vary between six and twelve months depending on the thermal load to which it has been submitted or if there has been frequent stopping producing the corresponding brisk changes in temperature. The reparation of one segment, three bricks high, takes between 20 and 30 hours. The rest of the cylindrical parts of the furnace can last from 24 to 36 months, the vault more than two years.

The black liquor after Venturi scrubber has a concentration 55 % and is sprayed by a rotating sprayer from the top of the smelter. The flue gases are leaving the smelter at the top and enter a waste heat boiler. The capacity of the smelter is 4.2 t dry solids per hour. The waste heat boiler is generating 14.5 t of steam per hour at 2.5 MPa (25 bar), 350 °C; 2 t/h are used for sootblowers. No auxiliary fuel is required. Before start-up the smelter is heated with wood. The smelter is placed on a concrete foundation on the floor and does not require a high steel structure. Details of the Epytek system were published on PAPEREX '95 and by Keswani (85).

4.4.6 Low temperature incineration in fluid bed reactors

Sodium carbonate (soda), the product of B.L. incineration, has a melting point 851 °C. In high temperature incineration the smelt temperature is held above 1000 °C to make the smelt fluid enough. In low temperature incineration the temperature is maintained below the melting point, which can be depressed by some non-process elements (see Chapter 2). Low temperature incineration is suitable for the soda pulping process as no reduction or Na_2SO_4 is required.

Lower temperature incineration has been applied in old rotary furnaces. However, incineration was incomplete. Far better combustion condition are in a fluid bed reactors as carbonated (charred) particles are completely combusted due to good mixing with air in the fluid bed. A prerequisite is a sufficient combustion temperature, which has to be balanced against the maximum temperature allowable from the standpoint of sintering (sticking) of particles resulting in big lumps and defluidization of the bed.

A typical fluid bed incinerator used in the pulp industry is the Copeland reactor used for incineration of NSSC (Neutral sulphite) and bagasse soda black liquor (34, 51). This system can incinerate waste liquor with as low concentration as 30 % (70 % water) and low heat value (12.5 MJ/kg dry solids) at a temperature of 650-730 °C. Such a simple system is shown on Fig. 13.

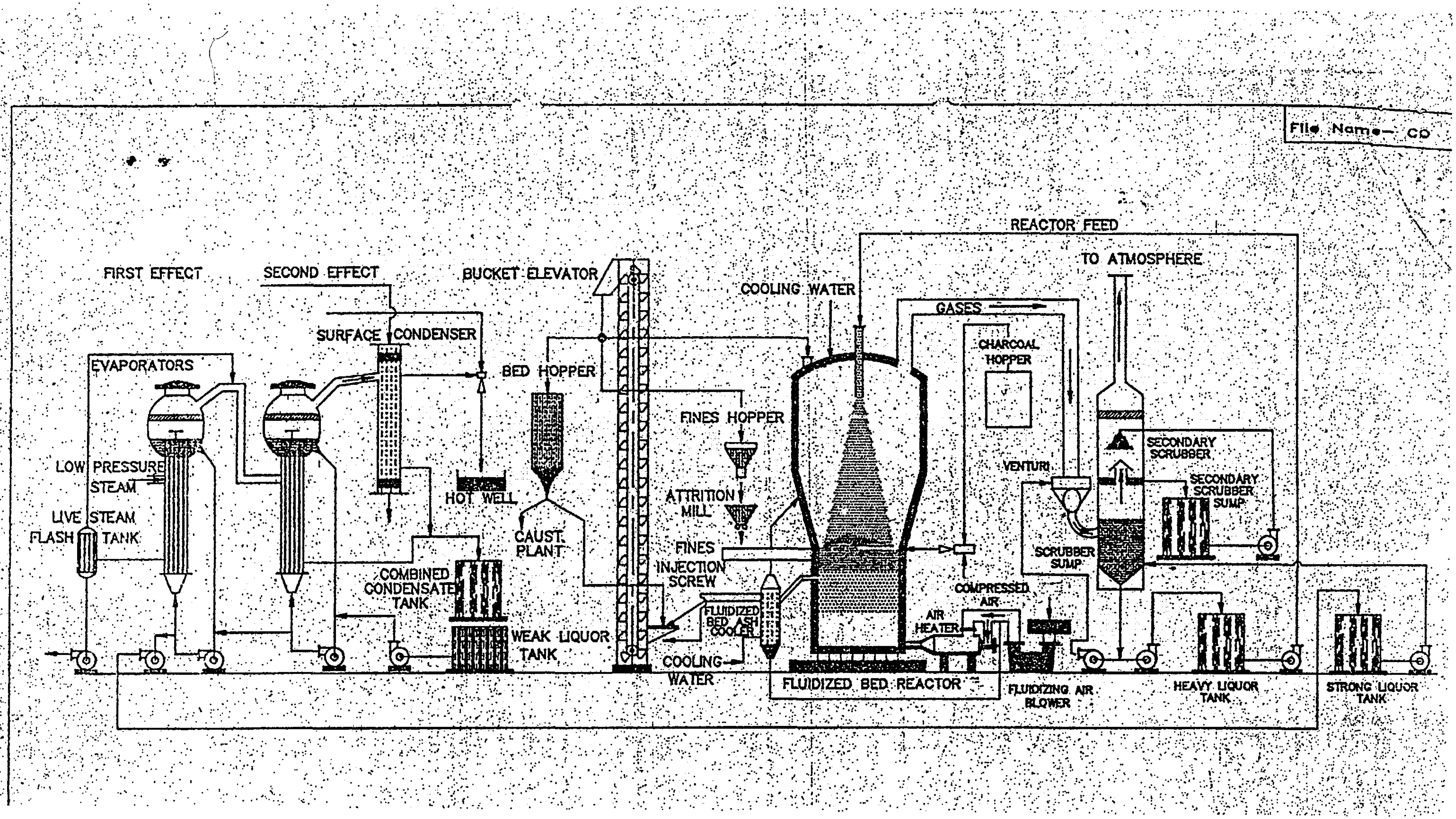


Fig.13
FLUIDIZED BED SODA RECOVERY SYSTEM
Source /15/

The evaporated black liquor is sprayed from the top of the fluid bed reactor. The droplets dry while falling down and are completely combusted in the fluid bed. The particles stick together forming pellets, which are continuously extracted from the bed. It is a common practice to operate the bed in soda units 30 °C below the fusion point.

A fluid bed reactor is a round-shaped refractory lined vessel consisting of 3 main sections :

A wind box where air is admitted to the reactor, separated by a distributor or orifice plate from the fluid bed zone, and a disengagement zone in the upper section (see Fig. 13). Air at about 0.5 kg/cm^2 is pumped into the wind box and passes through the orifice plate, which is designed to give complete dissemination of air over the entire cross sectional area of the plate, into the fluid bed zone. All combustion takes place in the fluid bed zone which consists of residual inorganics recovered by combustion from the waste liquors. By special design of the plate, the inorganic salts are caused to pelletize.

The dispersed air passes through the fluid bed particles and causes them to take on heterogenous motion and sets up a continuous violent mixing action on pellets, air and combustibles. The bed increases in volume by about 30 % and the particles are said to take on a fluid motion. In this state, the bed particles obey most of the hydraulic laws (e.g. exert a hydraulic head, will seek their own level, etc.) and the bed itself resembles a body of boiling water. Combustion is a surface phenomena and there is no visible flame. The whole mass of fluid bed glows at the temperatures normally used. No auxiliary fuel is needed, except for start-up.

Air passing through the bed is heated to bed temperature, the oxygen in the air is consumed in combustion of organics, and the gas leaving the bed is basically CO_2 and N_2. The free-board theoretically reaches the same temperature as the fluid bed zone and gas leaving the reactor will carry all products of combustion, some dust, and heat not lost through radiation or bed discharge pellets.

In the Copeland system the heat content of the exit gas is put to work and the freeboard zone becomes a simple heat exchanger. By injecting low concentration black liquor into the upper section of the reactor freeboard (countercurrently to the flow of exit gas) some or all of the water contained in the feed is evaporated and leaves with the exit gas, with the partially dried or dried liquor solids falling into the bed to maintain combustion.

The temperature of the freeboard zone is thereby decreased by ± 100 °C, but the efficiency of the fluid bed zone is increased proportionately by having less water to burn out. If, on the other hand, liquor is pumped directly into the bed zone, the water content exerts a cooling effect on the system and a much higher percent solids in liquor must be used if the system is to operate without auxiliary fuel.

A further beneficial effect results from freeboard feed additions. That is that the countercurrent flow of liquor against exit gas causes the incoming liquor to exert a scrubbing action on the exit gas and greatly reduces the dust carry over in the exit gas. By forcing dust particles to fall back into the bed zone, substantial savings in sensible heat losses are thereby affected and the dust collection problem is less serious.

The bed is sometimes cooled by injection of water in order to prevent overheating and lumps building. The flue gases are carrying some fly ash, which is separated in cyclones and finally in a scrubber using weak waste liquor, which is partly evaporated prior to entering the evaporator.

The advantages of this system is its simplicity and possibility to incinerate low-concentrated waste liquor. The heat economy is low, as the flue gases can be used for hot water only, but in some case a waste heat boiler was added.

In further development of this system higher concentration waste liquor may used making it possible to generate some low pressure steam for evaporators. However, there is a danger of overheating the bed and there are attempts to cool the bed by water coils connected to the steam generation system. This has reportedly good results as heat transfer in the turbulent fluid bed is higher than in flue gases. No such installation have been identified in bagasse mills.

The fluid bed reactor is frequently used in bagasse soda mills, but also in wood-based soda-anthraquinone pulping. In 1985 there were 28 Copeland reactors, half of them for bagasse black liquor incineration.

Two bagasse mills using a Copeland fluid bed reactor have been described (15) recently. The salient features of these mills are

	SAPI Stanger mill South Africa	Kimberley Clark Mexico
B.L. dry solids t/day	180-220	340
Recovered NaOH t/day	63	80
Weak B.L. concentration % DS	11-12	8-8.5
Evaporator	4 effect (5 body)	4 effect 4 body
Semi-concentrated B.L. % DS	25	26.5
Concentration B.L. after Venturi %	47	38
Fluid bed reactor diameter m		5.8
Bed depth cm	152	127
Bed temperature °C	700-715	710
Fire board temp °C	680	450
Fluidizing air flow m^3/min	22,000	30,000
Air pressure kPa	40	40
Chlorides %	< 0.35	> 0.5

The chemical recovery efficiency is about 95 %.

The reactor is stopped for cleaning 2-3 times a year. The reactor loading is 350-570 kg B.L. dry solids/m^2.h . The B.L. gun pressure is about 200 kPa, evaporator loading (evaporated water per unit surface) is high.

A fluid bed incineration requires only low concentration of black liquor (35 -

45 % for bagasse) and, consequently B.L. has to be evaporated in indirect evaporators only to 20-25 % concentration At this concentration scaling and viscosity is low and therefore the operation is smooth. However, the process requires a more thorough control when compared to a conventional recovery boiler. The basic principle of the process is pelletisation of inorganic compounds by fluidisation at temperatures close to their fusion temperature. This depends upon contamination of soda ash with other compounds mainly potassium compounds and chlorides. Contamination is a result of fibrous raw material composition but purity of make-up soda is also important.

One fluid bed reactor for incineration of wheat straw black liquor was installed in a pulp mill in Syria. This reactor was never in steady operation due to various reasons. One of the reasons for failure to operate was defluidisation of the fluid bed due to forming of lumps as a result of low melting point eutectics caused by high level of potassium (1.7 %) and chloride (0.25-0.5 %) in the straw (8). However during the extended periods (48 hrs) the bed was maintained at 640-690 °C i.e. the eutectics did not always limit operation to low temperature, where combustion is difficult. Lumps were formed even at low temperature (say 550 °C). It is assumed, that probably due to very high viscosity the liquor is leaving the spray nozzle sometimes as a much narrower concentration than intended. This may lead to local overloading of the bed with fuel and unter and this may result in a number of adverse effects including either localized overheating or cooling of the bed. Obviously more development work is required to improve the incineration of wheat straw black liquors in a fluid bed reactor. One of the possibilities is to add lime (CaO) to the bed to bind chlorides. This is used in incineration of high chloride containing wastes (35).

The Copeland system is in USA manufactured and marketed by Enders Process Equipment Corporation and in India Agro Pulping Machinery Ltd (see Annex II.). A recovery is ordered for a bagasse pulp mill of M/S Shreyans Ind. Ltd (Punjab). The system is using fuel oil and charcoal to heat the bed (Fig. 13).

A more sophisticated system is the Dorr-Oliver Fluosolid System in which the waste liquor of 40 % concentration is injected into the bed and the pellets of sodium salts are cooled in the lower part of the reactor in a cooling fluid bed. The weak waste liquor is evaporated in a indirect evaporator just to 20 % total solids and further in the Venturi-scrubber evaporator with hot flue gases. The incineration temperature is slightly higher, than in the Copeland process (35).

4.4.7 Other incineration systems

Recently the TSK Waste Liquid Combustion System has been developed by Tsukisima Kokai (Japan). It is basically a vertical combustion chamber, which can be operated and high or at low temperature. For pulping black liquors low temperature incineration is recommended (about 700 °C), without generating any smelt in the reactor. The black liquor is atomized in two injectors. Auxiliary fuel can be used from the top. The incinerator is used for sodium salts containing waste liquors. The incinerator can be operated at oxidative and reductive conditions. For self sustained incineration (without auxiliary fuel) black liquor of 40% concentration is required. According information from the manufacturer there are some installations in Japan working in reduction atmosphere. One installation was in Thailand for bagasse soda B.L. recovery. This system was recently replaced by a Tampella recovery boiler. No published data available about TSK system, but a company booklet is available in UNIDO.

The Sulzer system combined high and low temperature incineration. The black liquor was atomized by compressed air in two atomizers on the top of a vertical incinerator and was heated for a short time to a temperature higher than the melting point. The fine particles were stitching to larger ones and cooled by recycled cooler air to temperature below melting point in a mixing chamber and finally the incineration process was completed in a vertical boiler chamber. The process was installed in France, but operation was discontinued (53, 54).

4.4.8 Comparative evaluation of incineration equipment and conditions

Bagasse black liquor incineration under various condition was calculated and the following variables have been compared :

- black liquor firing concentration (52-75 %)
- evaporation of black liquor in multiple effect evaporator and combination of MEE with contact evaporator
- combustion air temperature (130-220 °C)
- waterwall (membrane wall) and refractory lined smelter
- operation with sootblowing and without sootblowing

For these calculations a bagasse black liquor with a HHV 13.0 MJ/kg dry solids was considered. For the calculation of a waterwall boiler a Tampella recovery boiler-smelter was selected. The design capacity of this boiler was 72 t/day dry solids (dimension 3.0 x 3.1 m) i.e. with low dry solids loading. For calculations of a refractory lined smelter the smelter in the Portela mill (Brazil) was considered (see page 52-53). The temperature of the smelt was considered 950 °C. The temperature of the black liquor was calculated as 100 °C. For sootblowing saturated steam from the boiler drum was considered and the heat calculated as input into the boiler. The losses from the boiler are such as heat for evaporation of water from black liquor, losses with smelt and other losses as radiation, non-combusted particles are included into efficiency calculations. The temperature of boiler feed water was considered 105 °C, temperature of ambient 25 °C. The results of calculations are in Table 21A, 21B. Output is in kg/h or in kW, specific data kJ/kg dry solids.

The adiabatic flame temperature was calculated as a sum of B.L. low heat value and enthalpy of combustion air (column "E"). It is important especially at low black liquor concentrations as at low adiabatic temperature the incineration of black liquor has to be supported by auxiliary fuel otherwise black-outs may occur. The adiabatic temperature should be by 350 °C higher than smelt temperature, which for silica containing black liquors is considered to be 950 °C. This was identified for incineration of black liquor at 52 % concentration in a waterwall boiler, where the calculated adiabatic temperature was 1,267 °C only (alternatives 1 to 4). In an air cooled refractory lined smelter the adiabatic flame temperature is 1,351 °C, i.e. by 50 °C higher (alternative 5, column "E") when compared with a waterwall boiler (alternative 1-4, column "E"). In an air cooled, refractory lined smelter there is no danger of black-out even at low black liquor concentration. In a waterwall boiler the adiabatic temperature at low B.L. concentration can be increased by auxiliary fuel (fuel oil) or by heating the combustion air to a higher temperature (alternative 6, 7) by steam. However, the combustion efficiency (column "K") is slightly less than for the refractory lined smelter (alternative 5). At a B.L. concentration 60 % the adiabatic temperature even in a waterwall boiler is over 1400 °C, but even in this case the adiabatic temperature in a refractory lined air cooled smelter is about 50 °C higher.

The flue gas temperature after the hearth (column "F") for water-wall boiler is the value calculated from the TAMPELLA smelter heat balance calculations. For the refractory lined smelter the temperature is much higher than in a water-wall boiler, as in a water-wall boiler much more heat is extracted from the hearth. The corresponding heat extracted from the hearth is shown in column "G". Column "H" shows the percentage of latent heat delivered to the water in the water-walls (i``-i`). In a refractory lined smelter the B.L. droplets are quickly dried.

The flue gas temperature before the contact evaporator (column "I") was calculated from the heat balance and parameters of the contact evaporators.

Data in columns "J" and "M" are expressing the boiler efficiency in % based on gross production of steam, which includes steam utilization for air and black liquor heating (Table 21B) and related to LHV (low heat value) of black liquor solids. Boiler efficiency based on HHV (high heat value) are in columns "K" and "N". Boiler efficiency after contact evaporator includes the heat required for evaporation of water in the contact evaporator and therefore boiler efficiency calculated after contact evaporator is higher. Boiler efficiency data are higher, than thermal efficiency data based on net steam production related to HHV of black liquor solids (column "O").

Sootblowing reduces net steam production and thermal efficiency (compare alternatives 1 and 2; 8 and 9). Black liquor evaporated in contact evaporator is cooled down by water evaporation and requires steam for re-heating to 100 °C (column "U"). The flue gases temperature in the alternatives with contact evaporator has to be higher as heat is required for water evaporation. Consequently, less steam is produced and boiler efficiency is less than without contact evaporator and evaporating B.L. on MEE evaporators only (compare alternatives 3 and 4; 9 and 10). Black liquor evaporated on

MEE evaporators only does not require reheating by steam (see column "U").

From the data in Table 21A and B can be concluded :

- steam for sootblowing reduces thermal efficiency by about 3 points (alternatives 1 - 2 and 8 - 9)
- preheating air in the walls of refractory lined smelter is more efficient, than preheating air by steam. The difference is about 2 points in thermal efficiency (alternatives 5 - 6 and 10 - 11)
- concentration of black liquor in MEE evaporator train instead of concentrating in direct contact evaporator increases thermal efficiency. However, this has to be corrected by steam required for concentration in MEE instead of direct contact evaporator (see " Overall thermal balance ")
- The most important factor is black liquor firing concentration. Increase from 52 % to 60 % concentration increases thermal efficiency by about 4.5 points when evaporated on MEE only (alternatives 4 - 9 and 5 - 11).

The most important possibility to increase thermal efficiency is to evaporate black liquor on MEE line to a concentration of 60 - 65 %. This may be possible with new types of falling film evaporators, but in some cases desilication prior to evaporation may be necessary. For evaporation to 65 - 75 % heat treatment of black liquor will be necessary to reduce viscosity.

The overall steam balance of the recovery system (Table 22) includes steam consumption for black liquor evaporation. Selected alternatives are presented in Table 22.

Table 21/A

COMPARISON OF VARIOUS INCINERATION CONDITIONS (BAGASSE BLACK LIQUOR), 3t/h DRY SOLIDS, 13 MJ/kg

Alternative	Boiler type	B.L. conc. %	Incineration air temp. °C	Adiabatic flame temp. ϑ_{ad}	Flue gases temp. after hearth ϑ_{sp}	Heat extracted from hearth kW	Percentage of latent heat delivered in incineration chamber	Flue gases temp. before contact evaporator °C	Boiler efficiency related to LHV before CE η_k	Boiler efficiency related to HHV before CE η_k	Evapor. in contact evapor. from-to %	Boiler efficiency for LHV after CE η_k	Boiler efficiency for HHV after CE η_k	Thermal efficiency %
1	WW	52	130	1,267.8	650-700	4,322-3,994	60.28	231.28	73.08	56.55	45>52	78.27	60.56	56.0 *
2	WW	52	130	1,267.8	650-700	4,322-3,994	60.24	226.95	72.74	56.35	45>52	77.86	60.32	52.7
3	WW	52	130	1,267.8	650-700	4,322-3,994	90.36	227.68	72.87	56.48	45>52	77.99	60.46	53.2
4	WW	52	130	1,267.8	650-700	4,322-3,994	84.39	-	77.99	60.46	-	77.99	60.46	57.8
5	RL	52	210	1,315.4	1,222	700	air heating	-	80.34	62.72	-	80.34	62.72	59.7
6	WW	52	200	1,301.7	650-700	4,576-4,248	86.35	-	78.45	61.19	-	78.45	61.19	57.6
7	WW	52	220	1,311.4	650-700	4,649-4,321	86.89	-	78.58	61.40	-	78.58	61.40	57.4
8	WW	60	130	1,412.5	650-700	5,027-4,722	69.81	322.26	70.05	57.24	45>60	79.92	65.30	56.4 *
9	WW	60	130	1,412.5	650-700	5,027-4,722	69.71	311.92	69.78	57.07	45>60	79.49	65.02	53.1
10	WW	60	130	1,412.5	650-700	5,027-4,722	91.73	-	79.63	65.16	-	79.63	65.16	62.1
11	RL	60	210	1,462.1	1,364	700	air heating	-	81.81	67.32	-	81.81	67.32	64.0
12	WW	65	130	1,491.7	650-700	5,400-5,110	97.76	184.56	78.47	65.92	60>65	80.39	67.53	62.26
13	WW	65	130	1,491.7	650-700	5,400-5,110	95.42	-	80.39	67.53	-	80.39	67.53	64.3
14	WW	75	130	1,629.6	650-700	5,940-5,667	99.90	-	81.54	71.36	-	81.54	71.36	67.7
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O

WW - Waterwall boiler RL - Refractory lined smelter B.L. - Black liquor CE - Contact evaporator Heat for evaporation of B.L. in CE is 2260 kJ/kg water * - without sootblowing

Table 21/B

STEAM DATA AND PRODUCTION / CONSUMPTION									
Alter native	Outlet pressure [MPa]	Outlet temp. [°C]	Gross steam production [kg/h]	Steam for air heating [kg/h]	Steam for B.L. heating [kg/h]	Nett available steam [kg/h]	Heat in steam [kW]	Heat for steam generation [kJ/kg_{DS}]	Note
1	0.6	158.83	10,117.69	598.51	94.8	9,424.38	6,070.85	7,285.04	NS
2	0.6	158.83	9,552.2	598.51	94.8	8,858.89	5,706.58	6,847.92	S
3	4.2	430	7,877.86	489.01	77.46	7,311.39	5,764.42	6,917.33	S
4	4.2	430	8,435.33	489.01	0	7,946.32	6,265.01	7,518.04	S
5	4.2	430	(9,066.12)[1]	(865.3)*	0	8,200.82	6,465.66	7,758.83	S
6	4.2	430	8,727.80	817.98	0	7,909.82	6,236.23	7,483.51	S
7	4.2	430	8,812.01	912.69	0	7,899.32	6,227.96	7,473.58	S
8	0.6	158.83	10,162.1	598.51	75.31	9,488.31	6,112.03	7,334.46	NS
9	0.6	158.83	9,600.81	598.51	75.31	8,926.99	5,750.44	6,900.56	S
10	4.2	430	9,025.78	489.01	0	8,536.77	6,730.53	8,076.67	S
11	4.2	430	(9,661.66)[1]	(865.3)*	0	8,796.36	6,935.20	8,322.27	S
12	4.2	430	9,097.18	489.01	53.57	8,554.60	6,744.59	8,093.54	S
13	4.2	430	9,320.88	489.01	0	8,831.87	6,963.19	8,355.87	S
14	4.2	430	9,792.76	489.01	0	9,303.75	7,335.23	8,802.31	S
A	**P**	**R**	**S**	**T**	**U**	**V**	**W**	**X**	**Y**

S - Sootblowing NS - without sootblowing B.L. - Black liquor

[1] - Fictions gross steam production includes steam equivalent to air heating in refractory walls

* - air heated in refractory walls of smelter - the value of heat equivalent to steam

Table 22

HEAT AND STEAM BALANCE OF RECOVERY SYSTEM FOR 1 TON DRY SOLIDS / H Alternative 2, bagasse B.L., HHV 13 MJ/kg								
Alternative	W.B.L. concentration %	B.L. concentration % after MEE	Evaporated water t/t dry solids	Steam economy t water evap / t steam	Steam available GJ/t dry solids	Steam for B.L. evaporation GJ/t	Steam surplus/deficit GJ/t dry solids	% Steam generated used for evap.
2A	10	45	7.78	3.2	6.84	5.43	+1.41	80 %
2B	10	45	7.78	4.2	6.84	4.14	+2.69	60 %
2C	8	45	10.28	3.2	6.84	7.18	- 0.34	Deficit
2D	8	45	10.28	4.2	6.84	5.47	+1.37	80.5 %

Note : 1. Steam 0.6 MPa generated in recovery boiler is reduced to 0.2 MPa in the mill steam system
2. No electricity co-generation

The steam balance shown in Table 22 is based on the most simple alternative 2 of black liquor incineration - evaporation on MEE to 45 % concentration, in direct contact evaporator to 52 % concentration, steam pressure 0.6 MPa. The data in this table emphasizes the importance of initial B.L. concentration and steam economy of the MEE. At 10 % concentration of weak black liquor there is a slight surplus of 0.6 MPa steam when compared with steam generated (available) at both steam economy levels. At 8 % concentration of W.B.L. there is a deficit of steam at a steam economy of evaporation 3.2 and a slight surplus at steam economy 4.2 . However, even is cases of surplus 60 to 80 % of the steam generated is used for evaporation even without electricity co-generation. In wood pulp mills only 20 to 30 % of steam generated is used for black liquor evaporation, if the B.L. is evaporated to 62-65 % concentration.

The steam surplus in an agro-based pulp mill with electricity co-generation is even less as shown in Table 23. Alternative 3 is the same as 2 with the difference, that the steam pressure is 4.2 MPa and is used for electricity co-generation (see 4.4.9). Naturally the steam surplus at same conditions is less with electricity co-generation (alternative 2A against 3A and 2B against 3B, Tables 21A and 21B). Increasing B.L. evaporation on MEE to 60 % concentration increases surplus steam, but even under these conditions at W.B.L. concentration 8% and 3.2 steam economy there is a deficit of steam. Even at highest steam surplus calculated at B.L. firing concentration 60 % and 4.2 steam economy nearly 70 % of the steam generated is used for B.L. evaporation. The reasons for this low overall heat economy of chemical recovery from agro-based black liquor when compared with wood black liquor are in order of importance :

- low concentration of weak black liquor (after pulp washing)

- low firing concentration of black liquor resulting in low thermal efficiency of incineration
- low steam economy of black liquor evaporation.

Possibilities for improvement of these sub-processes are discussed in section 4.2 and 4.3 .

Table 23

HEAT AND CO-GENERATED ELECTRICITY BALANCE
of recovery system for 1 ton dry solids / h , HHV 13 MJ/kg , 4.2 MPa steam 427 °C

Alternative	Steam generated		Electricity	Steam available GJ	W.B.L. conc. %	B.L. conc. % after MEE	Evap. water t/t	Steam economy t water /t steam	Steam for evaporation GJ/t	Steam surplus/ deficit GJ/t
	t/t	GJ/t	kWh/t							
3A	2.43	6.91	230	5.83	10	45	7.78	3.2	5.43	+0.4
3B	2.43	6.91	230	5.83	10	45	7.78	4.2	4.14	+1.69
3C	2.43	6.91	230	5.83	8	45	10.28	3.2	7.18	- 1.35
3D	2.43	6.91	230	5.83	8	45	10.28	4.2	5.47	+0.36
5A	2.73	7.75	259	6.55	10	52	8.07	3.2	5.63	+0.92
5B	2.73	7.75	259	6.55	10	52	8.07	4.2	4.29	+2.26
11A	2.93	8.32	278	7.03	10	60	8.3	3.2	5.79	+1.24
11B	2.93	8.32	278	7.03	10	60	8.3	4.2	4.41	+2.62
11C	2.93	8.32	278	7.03	8	60	10.83	3.2	7.56	- 0.53
11D	2.93	8.32	278	7.03	8	60	10.83	4.2	5.76	+1.27

Note 1 : 95 kW/t steam or 4.64 GJ/MW. Back pressure steam 0.5 MPa
Alternative 3, 4 - B.L. firing concentration 52 %
Alternative 11 - B.L. firing concentration 60 %

4.4.9 Possibilities of electrical energy co-generation

Electricity co-generation is an integral part of the recovery system in large pulp mills. None of the reviewed Chinese small mills has electrical energy co-generation, as MP steam is generated. One of the two Indian small pulp mills is generating 4.0 MPa steam and co-generating el. energy in an extraction - back pressure turbine together with boiler plant steam (25 % extraction 1.2 MPa, 75 back pressure 0.4 MPa). The other Indian mill has a recovery boiler without superheater and economizer and is generating 1.6 MPa steam. This is actually a waste heat steam boiler. High pressure steam boilers (4.0-6.0 MPa) are by about 17 % more expensive. Electricity co-generation requires a more sophisticated and more expensive recovery boiler in addition to a steam turbogenerator.

To evaluate approximatively the economy of electrical co-generation data and budgetary prices of small steam turbogenerators manufacture in India have been obtained courtesy of M/S Chemprojects, New Delhi. The data of the recovery boilers under consideration are specified in Table 23. The steam pressure considered is 4.2 MPa. Back pressure turbogenerator with outlet pressure 0.5 MPa was considered. No extraction is anticipated as 65 % or more steam is used for evaporation according evaporation conditions. According manufactures data the electrical energy co-generation is 95 kW/t steam.

The heat consumption was calculated 4.64 GJ/MW, which is higher than in large turbogenerators (about 4.0 GJ/MW) of extraction - back pressure type. The overall steam balance including evaporation calculated from the above mentioned data is specified in Table 23. It is evident, that the surplus steam is less, than without electricity co-generation and there is a deficit at 8 % weak black liquor concentration and 3.2 evaporation steam economy even at B.L. firing concentration 60 %. As the steam surplus at weak black liquor concentration 10 % is also low no extraction of MP steam was considered and it is anticipated that the surplus steam remaining after supplying evaporators will be used in the bleach plant or paper mill. Back pressure turbogenerators are cheaper than extraction - condensing type or double extraction - condensing type.

The data of turbogenerators in the range 1-2.5 MW and the cost calculations are summarized in Table 24. The calculations are based on the budgetary price of turbogenerators and the estimated difference between simple waste heat boilers without economizer and superheaters which is about 17 % of the recovery boiler budgetary price. The total investment cost is the sum of turbogenerator price and recovery boiler price increase plus 30 % for erection, engineering, civil works etc. Maintenance costs were calculated as 6 % of total investment cost. Labour costs included 2 operators (out of this one foreman) in 4 shifts totalling USD 13,494 per annum. Depreciation was calculated 12 % on investment costs, interest rate 15 % i.e. capital cost 27 %. The calculated manufacturing cost of 1 MW included price of steam (see Chapter 7) consumed and was compared with price of electricity (see Chapter 7).

The difference between manufacturing price per MW electricity and average market (grid) price per MW multiplied by total electricity production are the net savings (profit). The pay-back period was calculated by dividing total investment cost by total net savings. The manufacturing cost and pay-back period was calculated in two alternatives. Alternative "A" is based on 90 % capacity utilization and 8,100 production hours per year, alternative "B" on 100 % capacity utilization and 8,300 production hours per year. In both cases the average price of steam and electricity was applied (see Chapter 7). The results are presented in Table 24. The table shows that recovery boiler price increase (for generation of high pressure steam) is higher than the price of the corresponding turbogenerator (based on Indian prices).

The manufacturing cost of co-generated electricity even at 1 MW capacity are

Table 24

APROXIMATIVE FEASIBILITY CALCULATION OF EL. CO-GENERATION
in Indian conditions

Turbine / Alternator capacity	Inlet steam	Corresponding to		Turbogenerator budgetary price 1,000		Recovery boiler price increase	Total investment cost	Capital cost	Maintenance labour	Manufacturing cost USD/MW		Pay-back period years	
	t/h	dry solids TPD	pulp TPD	INR	USD	1000 USD	1000 USD	1000 USD	USD /a	A	B	A	B
1 MW	10.5	86- 92	60- 65	7,750	235	340	747	201	58,318	69.9	65.8	11.5	6.8
1.5 MW	15.75	129-138	107-115	8,000	243	440	861	232	65,154	61.3	58.2	4.6	3.4
2 MW	22.0	180-193	130-150	8,000	243	500	964	260	71,334	57.1	54.3	3.0	2.4
2.5 MW	26.25	215-230	155-190	9,500	288	550	1,089	294	78,834	54.8	52.3	2.5	2.0

1 Additional investment (estimate) cost for 4.2 MPa against MP steam boiler
2 Including 30 % erection, civil, piping, contingency etc.
3 Maintenance 6 %, labour USD 13,494 /a
4 Steam price USD 7.57 /GJ i.e. USD 34.36 /MW electrical price USD 78.8 /MW (India)
A = 90 % capacity utilization, 8,100 hours per year
B = 100 % capacity utilization, 8,300 hours per year

lower, than the average price from the grid in India. However, when the lowest grid price is considered, than in alternative " A " the prices are equal at 2 MW capacity and at 1.5 MW capacity for alternative "B". In all cases manufacturing cost of co-generated electricity are lower, that maximum grid prices (USD 90.9 /MW). The manufacturing cost decrease with increasing capacity, but decrease is comparatively low.

Actually the manufacturing cost are heavily influenced by steam, as expenditure for steam is the major part of the manufacturing cost (calculated for Indian conditions, alternative "B")

	1 MW turbogenerator		2.5 MW turbogenerator	
	USD	%	USD	%
Capital cost	201,000	36.9	294,000	27
Maintenance, labour	58,314	10.7	78,834	7.26
Steam price	285,000	52.3	712,970	65.6

The economy of scale determines the pay-back period. For 1 MW turbine the pay-back period is beyond the level 5 years, but decreases significantly with increasing capacity of turbogenerator, when calculating average steam and electricity prices (in India). Electricity supply from public grid in India is non-reliable, with frequent power shedding, resulting in heavy disturbance of the recovery process. This was personally observed by the author of this study. It is therefore advisable to co-generate electricity even in small mill, where the pay-back period may exceed 5 years. The additional benefit of smooth operation using own co-generated electricity can not be exactly calculated, but certainly is attractive.

Energy prices are significantly lower in China (see Chapter 7). The steam price is 35-40 % of the Indian level and electricity 50-55 % of the Indian prices. No data about approx. prices of turbogenerators and recovery boilers in China are available. If we use the Indian approx. prices and Chinese average price for steam, than for a 1 MW turbogenerator the manufacturing price of electricity is USD 48.19 /MW which is equal to the higher grid electricity price in China for a 2.5 MW turbogenerator the manufacturing price is USD 33 /MW, i.e. USD 6.4 lower per MW as average grid price. Under these conditions the pay-back period is 9.3 years. This underlines the importance of steam and electricity price level for feasibility of co-generation.

The price for the turbogenerator is 35-40 % of the investment cost for co-generation (without erection and other cost). It is therefore useful to consider electricity co-generation from recovery boiler steam in the mill power station using the same turbogenerator for the power station steam a recovery boiler steam. This require adjustment of steam pressure and smooth operation of the recovery boiler.

4.5 Causticizing of green liquor and lime mud reburning

The smelt from the recovery boiler or the pellets from a fluid bed reactor is dissolved in water to green liquor. Green liquor from soda pulping contains sodium carbonate only and some non-process elements such potassium salts, silica, chlorides etc. The green liquor from sulphate (kraft) cooking contains beside sodium carbonate sodium sulphide. During the slaking operation sodium carbonate reacts with calcium oxid to form sodium hydroxide and calcium carbonate and the final solution is the white liquor

$$Na_2CO_3 + CaO + H_2O = 2\ NaOH + CaCO_3$$

Silica in the green liquor is in the form of sodium silicate and reacts :

$$Na_2SiO_3 + CaO + H_2O = 2\ NaOH + CaSiO_3$$

Neither of these reactions is quantitative.
The sodium carbonate causticizing reaction is expressed usually by following terms calculated as Na_2O

$$\text{Causticizing efficiency} = \frac{\text{NaOH (less NaOH in green liquor)}}{\text{NaOH - NaOH in green liquor} + Na_2CO_3}$$

$$\text{Causticity} = \frac{\text{NaOH}}{\text{TTA}}$$

TTA = Total titrable alkali = $NaOH + Na_2S + Na_2CO_3 + 1/2\ Na_2SO_3$

The lime mud i.e. the calcium carbonated formed in the causticizing process is reburned in a lime calciner to lime (CaO).

Silica is the most undesirable non-process element in the causticizing and lime reburning process. The influence of silica was investigated by Lengyel (25) and Kulkarni (55). The rate of sedimentation decreases and the volume of sediment increases with increasing silica content in green liquor. Causticity slightly increases with silica content as a great part of sodium silicate is converted to NaOH. Causticizing efficiency decreases and sludge dryness decreases with increasing silica content as shown in Table 25.

Table 25

CONVENTIONAL CAUSTICIZATION WITH VARYING AMOUNT OF SILICA IN GREEN LIQUOR						
Particulars / Alternative		0	1	2	3	4
Silica in green liquor,	%	Nil	0.5	1.5	3.5	5.5
Analysis of white liquor						
TTA as Na_2O,	gpl	90.36	90.72	91.44	92.88	94.22
Sodium hydroxide as Na_2O,	gpl	70.2	69.1	71.9	70.2	69.2
Causticity,	%	94.8	95.2	95.7	95.9	96.0
Causticization efficiency,	%	90.1	89.2	88.3	86.6	85.0
Suspended matter,	gpl	-	-	-	5.8	6.2
Analysis of lime sludge						
Sludge dryness,	%	47.9	43.2	41.7	37.2	35.9
Silica as SiO_2,	%	Nil	0.46	1.26	2.86	3.25

Source (55)

As a result of reduced sedimentation rate a large sedimentation surface/volume by 50-100 % is required for white liquor clarifiers. Lime mud is difficult to dewater. Sodium losses increase.

Silica in the lime reburning process combines with CaO to form calcium silicate. This forms a glass-like and dense coating over lime lumps, which do not react with water when slaked in weak wash liquor or water. During the calcination process overburned or underburned lime is produced if silica content in lime mud is too high. The calciner kiln has to be longer to make possible gradual burning of sludge at lower calcining temperature. The fuel demand of high silica containing lime mud is higher. Silica is binding CaO and, consequently, the purity (availability) of the burned lime is less. To keep availability on an acceptable level at high silica content in the green liquor a part of the lime mud has to be disposed of (purged) to keep silica content in lime mud on an acceptable level, i.e. 4-5 % (12). The amount of purged lime mud will depend on silica input into the system. The silica sources are the fibrous raw material, make-up chemicals (sodium sulphate) and make-up limestone. Benitez (60) investigated the material balance at different lime mud availability at 1 % silica in bagasse, 0.5 % silica in limestone (availability 85 %). The following material balance elements have been investigated (see Table 26).

Lime Mud Availability : This term refers to the purity of the lime mud.

Potential Lime Lost : These figures represent the amount of make-up lime needed to replace the calcium carbonate that is lost with the lime mud in order to keep the silica out. For this reason, it is called potential lime lost. Note that the availability of lime mud can be kept constant at any level - the lower the availability, the lower the make-up lime.

Limestone Make-up : These figures represent the quantity of limestone needed at each availability. They are directly proportional to the potential lime lost.

Lime Mud Removed : These figures represent the lime mud to be removed and are proportional to the potential lime lost. The quantities are considerably higher - over 65 % availability. This implies that the lime-mud disposal operation is more expensive at a higher range.

Lime Mud to Calciner : The quantity of lime mud shown at each availability contains the equivalent amount of calcium carbonate to produce the necessary lime required for one ton of pulp.

Total Lime Mud :These figures represent the lime mud present in the recausticizing cycle. Note that the total lime mud descends to its lowest point at 65 % availability, after which it again increases.

Calcinated Lime : These figures represent the amount of energy required by the lime to produce one ton of pulp at each availability.

Kiln (Calciner) Product : As a result of the impurities in the lime mud, the kiln product increases as availability decreases.

Silica in the Product : The percentage of silica in the product increases as availability decreases. This will play an important role in determining the feasibility of installing a calciner.

Table 26

LIME-MUD DISPOSAL OPERATION
MATERIAL BALANCE FOR ONE TON OF UNBLEACHED PULP
OPERATING BALANCE AT ONE-PERCENT SILICA IN THE BAGASSE

Lime Mud Availability %	75	70	65	60	55	50
Potential Lime Lost kg	112.5	70.65	49.5	36.45	28.35	21.6
Limestone Make-up kg	236.25	148.5	103.95	76.5	53.1	45.45
Lime Mud Removed kg (purged)	238.5	156.6	115.2	89.55	73.8	60.3
Lime Mud to Calciner kg	469.8	490.95	515.25	544.05	577.35	617.85
Lime Mud-Total kg	708.3	647.55	630.45	633.6	651.15	678.15
Lime Mud Removed % (purged)	34	24	18	14	11	9
Kiln Product kg	295.65	316.8	341.1	369.9	403.2	443.7
Silica in the Product %	6.1	7.2	8.4	9.6	10.8	12.0

Source (56) kg = Dry basis.

Data in the Table 26 indicate for a bagasse with 1 % silica content and limestone make-up with 85 % purity the lime disposal alternatives as follows :

- While operating at higher availabilities, the energy required in the process is lower, but the lime-mud disposal operation as well as required make-up are much higher.

- Another alternative that will reduce the amount of make-up and lime-mud disposal is to discharge a lesser amount of lime-mud; however, energy consumption will be higher.
- The third alternative is to send the lime-mud to an existing cement plant, when possible. Some mills in India transport lime-mud to cement plants. This practice will avoid a field disposal operation and maintain optimal lime availability when a calciner is under consideration.
- The last alternative is to calcine all of the lime-mud in order to produce excess lime. The excess lime sold as a byproduct will carry the silica away from the system, keeping availability also at is best level. This may be the best answer to the silica problem.

A thorough analysis of the lime-mud disposal operation and its alternatives must be done on a long-range basis. This can only be accomplished by tabulating all the essential elements, as in Table 26, using the exact amount of silica in the raw material. Otherwise, the installation of a calciner may be impractical and unprofitable.

The lime disposal (purging) in the above mentioned table is 34 % at 75 % availability. However, at a higher silica content in bagasse the disposal is higher. The Propal bagasse mill in Colombia purges 50 % of the lime mud.

4.5.1 Silica balance in the cooking and recovery cycle

Another approach is a complete material flow and silica balance by a computer-aided simulation. Such a simulation programme was developed for this study by J. Schmied. The silica balance takes into account all outlets :

- Silica output with pulp : this will vary in wide range depending on residual alkali in cooking (see Chapter 3).
- Losses in washing and other losses of black liquor.
- Spontaneous settling of silica sludge in B.L. tanks. This may be more important in small mills, where storage tanks are comparatively large and retention time long
- Silica scalings in evaporators, preheaters etc. are small outlets.
- Lime mud disposal (solid purge) or reburned lime disposal is the most important silica outlet.
- In case a desilication of black or green liquor will be installed this will be the most important outlet.

Silica is built up in the alkali cycle as the reaction of sodium silicate with calcium oxide is not quantitative (see section 3.2). In case of lime mud reburning silica is built up in the lime cycle. Solid purge of lime mud or reburned lime keeps silica content in acceptable limits. In wood black liquor recovery about 15 % of reburned lime is purged, usually the dust separated from calciner flue gases is purged. The problem is more serious with black liquor from agricultural residues or bamboo which contain high percentage of silica.

In the next flowsheets (Fig. 14, 15) the silica balance for 2 cases of bagasse black liquor recovery are presented. In both cases silica content in bagasse is 1.8 % which is lowered in depithing by 30 %. Bagasse pulp yield is 50 %, silica in pulp 1 %, in make-up limestone 2.5 %. The spontaneous desilication in tanks is 25 %. The required limestone is calculated on 100 % purity bases.

In case 1 the amount of solid purge is calculated to keep silica in lime mud on 4.5 % level.

In case 2 a 15 % solid purge and the required desilication efficiency of black liquor (see Chapter 6) is calculated.

In case 1 the required solid purge (lime mud disposal) is 58 %.

In case 2 the required desilication efficiency is 83.1 %. In this case limestone demand is 52.5 kg/t of pulp (on 100 % basis).

It is evident, that no general calculation of lime mud disposal is not possible as too many variables influence the material balance. The limit for the calciner may be also different. The silica limit for longer rotary kilns with more gentle reburning may be higher. On the other side black liquors and consequently green liquors from fibrous raw materials containing more silica will carry more silica into the causticizing process increasing silica in lime mud. In such cases lime reburning even with high percentage of solid purge is impossible.

The SEKA-Afyon straw pulp mill in Turkey is producing 50,000 ton pulp/a. The silica content in lime mud is about 12 % on dry solids basis. It is not possible to reburn this lime mud and the mill is disposing about 20,000 t/a lime mud.

It is advisable to calculate the silica material balance in order to determine for each case the how much lime mud can be reburned and how much has to be the solid purge (lime mud disposal) or what should be the required desilication efficiency. The silica balance computer programme is available with the author.

4.5.2 Feasibility of lime mud reburning

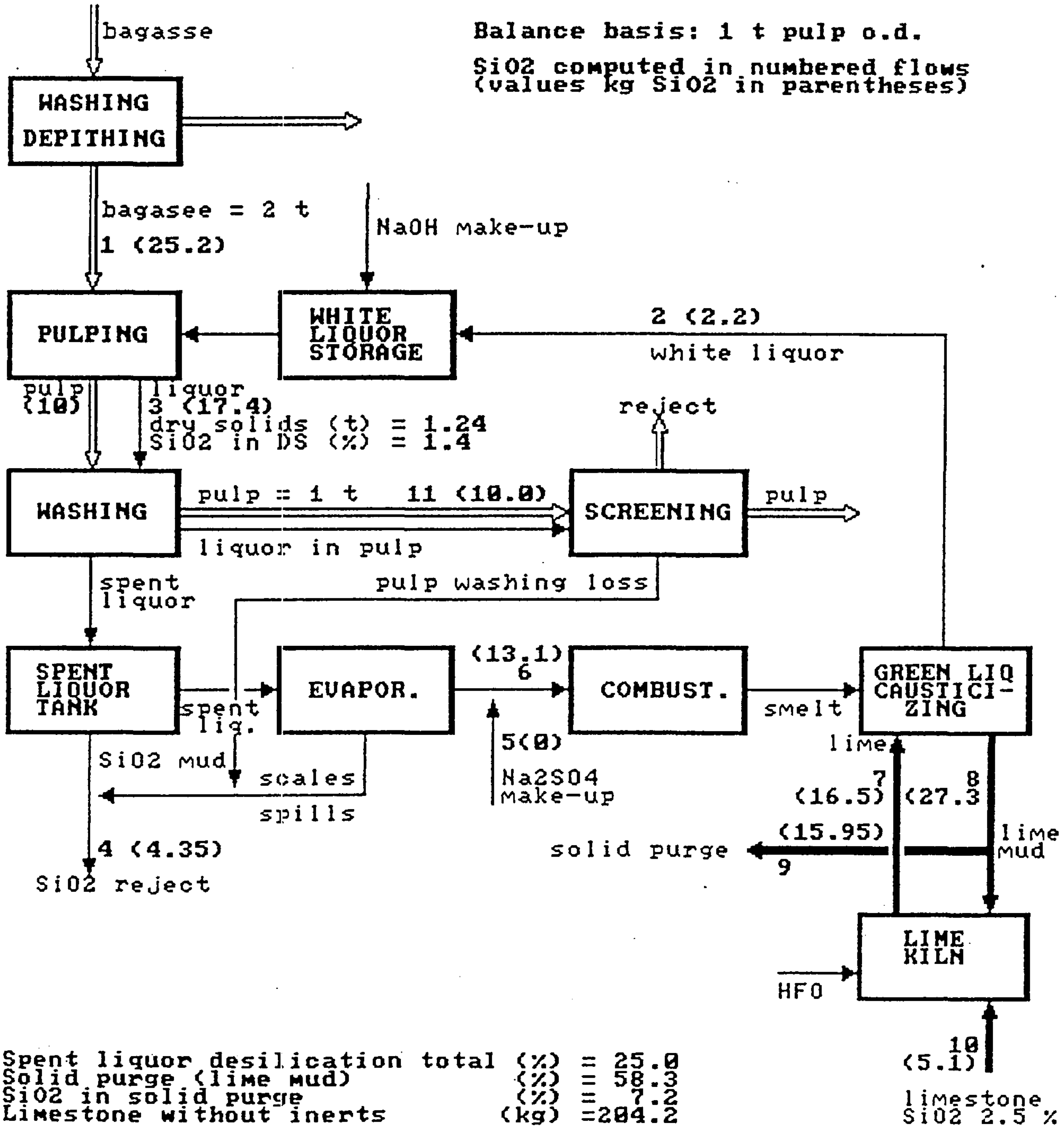
This will depend on relation of heavy fuel oil, limestone or quick lime (CaO) prices and transport costs of limestone/quick lime as transport costs of these cheap commodities have a heavy influence on feasibility. Two feasibility calculations for India conditions (52) on 1992-93 price level (HFO INR 4,300 /t, limestone INR 450 /t, lime INR 1,300 /t) indicate savings when using reburned lime of about INR 550-700 per ton of lime on manufacturing costs basis. For a mill of 160 TPD pulp capacity the total investment for a lime reburning plant in 1992 was estimated to be INR 36 million (USD 1.2 million), i.e. the pay back period was about 3-3.5 years discounting capital costs.

In China both fuel oil and limestone/quick lime prices are considerably lower (see table) and lime reburning in small pulp mills is not feasible.

Feasibility of lime reburning will be less in small mills due to economy of scale. High silica content will reduce amount of reburned lime decreasing feasibility of the process.

BASIC SILICA BALANCE OF A BAGASSE PULP MILL

Case 1: NO SPECIAL DESILICATION PROCESS INVOLVED

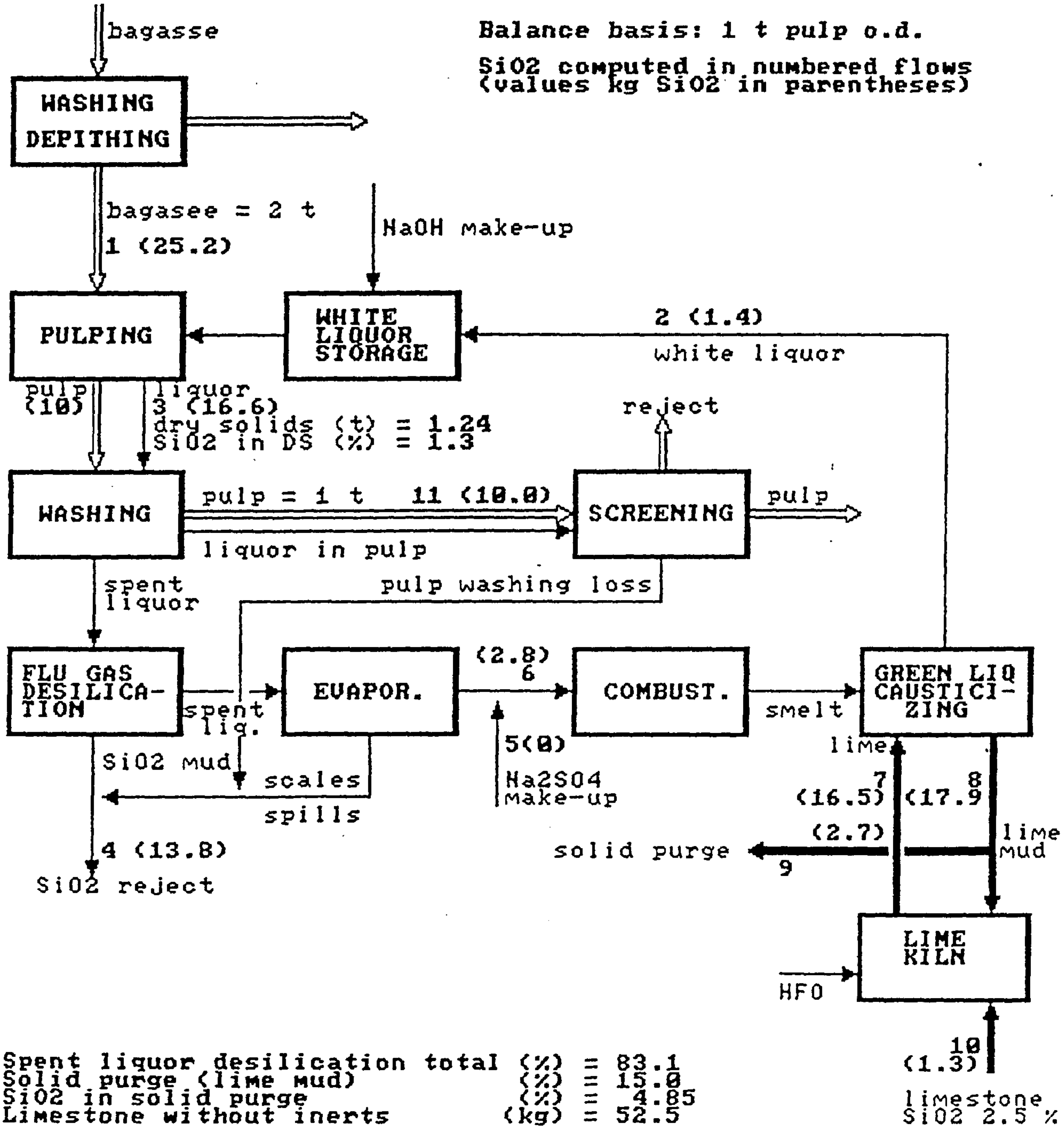


Spent liquor desilication total (%) = 25.0
Solid purge (lime mud) (%) = 58.3
SiO2 in solid purge (%) = 7.2
Limestone without inerts (kg) =204.2

Fig.14

BASIC SILICA BALANCE OF A BAGASSE PULP MILL

Case 2: FLUE GAS DESILICATION PROCESS INVOLVED



Spent liquor desilication total (%) = 83.1
Solid purge (lime mud) (%) = 15.0
SiO2 in solid purge (%) = 4.85
Limestone without inerts (kg) = 52.5

Fig.15

5. DESILICATION TECHNOLOGIES

5.1 Introduction

Various processes have been proposed to exclude silica from the cooking and chemical recovery process and thus to make pulping of non-wood fibrous raw materials especially straw more effective. Black liquor is the initial medium / input material of the chemical recovery system. Desilication of black liquor will eliminate or at least substantially depress all difficulties in the recovery system caused by silica. In some cases silica content in B.L. can be reduced by modifying cooking conditions (see section 2.2). Except of raw material cleaning and in one case green liquor desilication in the NACO process no mill with desilication was identified. Basically there are two possibilities to eliminate silica dissolved in alkaline solution i.e. in black liquor and green liquor :

- reduction of solubility and precipitation of silica by decreasing RAA and pH especially by carbonation with CO_2.
- reaction of sodium silicate with metallic ions (Ca, Al) resulting in insoluble silicates.

Neither of these reactions is quantitative.
Desilication methods have been reviewed by Panda (6b) and Bleier (23k).

5.2 Partial desilication by raw material cleaning

It is adviseable to reduce silica input into the recovery system by cleaning of fibrous raw material. Straw dedusting is a simple way of silica reduction, but not efficient enough.

Depithing of bagasse reduces silica in bagasse. Simultaneously the surface is cleaned from silica containing dust. Depithing is a standard operation in bagasse pulping.

Washing of bamboo chips eliminates according Panda (6b) about 50 % of silica. Similar equipment is used as in wood chip washing. This is applied in several bamboo pulp mills.

Wheat straw pretreatment is used in the Italian Foggia straw pulp mill (22). Straw bales are fed without chopping into a continuous NACO-pulper. Crude contaminants (metals, stones, plastic material) are continuously discharged from the pulper. The pretreated straw is pumped to a fluidification device to separate small contaminants and sand. 1-2 % alkali on straw (NaOH or Na_2CO_3 from recovery) is added and the defibrated material is washed and pressed to 25-30 % dry content. The yield range is 80-90 %, reduction of silica about 50 %. NaCl is also reduced, if content in straw is higher due to soil contamination. An additional benefit is, that the fibrous raw material is free from waxes and easy to impregnate with chemicals. The NACO cleaning process is included in a new Chinese mill project.

The Central Pulp and Paper Research Institute (India) tested (56) straw cleaning in pilot scale using a disc mill comprising of a stationary and a rotating disc with exchangeable grinding elements and a universal separator. By excluding fractions containing high silica about 50 % of silica could be removed. No information is available about application on mill scale.

5.3 Black liquor desilication methods

5.3.1 Spontaneous partial desilication of black liquor by storing (ageing)

When storing black liquor at elevated temperature residual alkali and pH decreases and silica together with some lignin precipitates. The following changes were determined by CPPRI :

Time of storage hrs	pH at 23 °C	RAA NaOH g/l	SiO_2 % w/w	TS % w/w
0	11.81	4.52	3.43	15.5
24	10.53	1.2	0.347	15.63

More detailed studies have been carried out in China (23d) using a 200 m^3 tank with a conc. After 8 hours at 80 °C the alkaline sulphate B.L. SiO_2 concentration decreased from 4-4.65 to 0.63-0.93 g/l in the clean liquor. The volume of sludge was 8 % of original containing 20.3 g/l SiO_2. In another experiment the sludge composition was as follows (Table 27).

Table 27

ITEM	CONTENTS %
ash	38.34
SiO_2 %	16.42
lignin %	12.78
incineration loss %	61.66
high heat value	4.4 MJ/kg solid

The desilication efficiency was about 80 %. The sludge (about 10 % of original solids) contained a significal amount of lignin and other organic substances (together about 60 %) i.e. about 10 % of organic substance is lost and can not be incinerated in a recovery boiler. Such spontaneous desilication may be useful in a small pulp mill, but pollution will be still high and sludge disposal probably difficult. This should be investigated more in detail.

5.3.2 Desilication of black liquor by lime addition

Gruen (57) investigated lime desilication at elevated temperature using excess of lime (up to 6 times of stochiometric quantity). Jayme (58) modified the process using semi-concentrated black liquor (30 % solids) and reduced lime to only twice the stochiometric quantity. This process was also investigated by West Coast Paper Mills in India (59). The desilication efficiency of the lime process is high (85-90 %), but the amount of sludge is large and some lignin may be co-precipitated. Calcium also reacts with organic acids of the black liquor resulting in heavy scaling of evaporators. The process was never applied in industrial scale.

5.3.3 Desilication by black liquor by carbonation

Basic principles

Black liquor is a complex colloidal solution or organic and inorganic compounds. The main component (about 50 %) is alkali lignin containing phenolic and carboxylic groups. These are in form of sodium phenolates and carboxylates i.e. in alkaline medium are hydrophilic and are keeping lignin in solution. Besides this B.L. contains hemicelluloses, sacharinic acids and inorganic components (sodium hydroxide, sodium salts and silica). Silica is in the form of sodium silicate. Both lignin and silica can be precipitated when lowering pH with acids. Carbonation with CO_2 was found by several authors (6b, 23k) as the only practical way to precipitate silica. Selective precipitation of silica is a very sensitive process as co-precipitation of lignin should be avoided. The phenolic groups of lignin in black liquor have an acidity in the range pK=9.4 to 10.8 (6c), whilst silicic acid value is between this i.e. pK 9.8 (6c). Nevertheless silica can be preferentially precipitated as silica forms by polymerization large molecules bound by covalent siloxane linkage (-Si-O-Si-). The high salt concentration of black liquor fravours silica gel formation rather than sols. The main problem is to attain by carbonation a pH which is very close to silica precipitation without over-carbonating i.e. lowering pH too much as this would cause lignin precipitation. Silica gels are difficult to filter and early attempts failed on filtration (23k). Franzreb (62) reported, that slow carbonation with flue gas improves filtration of silica gel. Some workers (63) added precipitated silica for nucleation. However silica dissolves quickly in alkaline black liquor and no tangible effect was achieved. Several companies and research teams were involved in development of desilication by carbonation in the eighties. The most comprehensive work has been carried out in 1970's and 1980's. Several research teams and companies have been involved in development of a suitable desilication technology by black liquor carbonization e.g. Lurgi, Kraftanlagen München and some mills. However, only the technology developed by the Central Pulp and Paper Research Institute (India) (CPPRI) in co-operation with UNIDO and SIDA has reached to an operating level within reasonable limits. The results of the CPPRI / UNIDO / SIDA project were published in detail in the Proceedings of the International Seminar on Desilication, Cochin (India) Dec. 1989 (available with UNIDO) (6).

The main results of investigations in laboratory and bench scale desilication of bamboo B.L. are as follows :

Direct carbonation with CO_2 (bubbling of CO_2) :
Better filtration was obtained by flue gas i.e. gentle carbonation rather than with 100 % CO_2. SiO_2 removal up to 90 % was achieved, but sludge contained high percentage of organics.

Carbonation in packed columns showed some difficulties :

- Heavy foam formation
- Localized carbonation leading to lignin and silica precipitation. Carbonation was not gentle. Uneven carbonation - portions of B.L. drained along wall not carbonated
- Poor filtration of sludge due to foam formation

The results indicated that gentle, slow carbonation has to be applied to achieve high desilication efficiency good filtration and selective desilication.

Carbonation in submerged bubble reactor (SBR) proved to be most efficient. SBR is illustrated in Fig. 16. In the reactor, the liquor to be treated with CO_2 is circulated through a pump in a tubular system. The CO_2 gas is at the upper limb of the tube. The liquid on its downward path sucks in gas in the form of discreet bubbles. The shearing action of the flow works that the bubbles in a kneading fashion continues exposing new gas-liquid interfaces results in slow reduction of pH. It is general observed that even at 90 % desilication silica sludge was almost white in colour organic matter was significantly low. Best results are obtained with stepwise carbonation as shown in Table 28 (laboratory experiments)

Table 28

RESULT OF STEPWISE CARBONATION IN SBR (BAMBOO B.L.)

Expt.	Initial liquor		Desilicated liquor			Sludge	
No.	pH 30 °C	SiO_2 g/l	pH 30 °C	SiO_2 g/l	Desilication %	Organics % *	SiO_2 %
1.	12.65	7.5	10.7	2.2	71	2.2	82
2.	12.29	7.9	10.5	1.2	85	1.3	90
3.	12.66	7.5	10.6	2.1	72	-	89
4.	12.30	8.5	10.7	2.4	71	1.7	84

Source (64)

* Determined by colorimeter (washed sludge)

Realkalisation and decarbonation : Carbonation and lowering pH to 10.1-10.3 actually consumes residual alkali of black liquor. During evaporation of carbonated B.L. lignin may precipitate. Viscosity of carbonated B.L. is much higher (more than double). Realkalisation is necessary. Although lime (CaO) was tested caustic soda is recommended. Viscosity was reduced to nearly the original values. By realkalisation with caustic soda the increase of residual alkali is not proportional to the added NaOH as some NaOH consumed by the sodium bicarbonate. Decarbonation by boiling carbonated black liquor under vacuum is a way to reduce caustic soda charge in realkalisation.

Desilication of black liquor from a mixture of wheat straw and reed (70:30) in laboratory and semipilot plant scale confirmed suitability of this process especially using SBR reactor. A silica removal up to 90-95 % was achieved (7).

5.3.4 Desilication plant in Hindustan Newsprint (HNL) Ltd (India)

Based on CPPRI - UNIDO development work a desilication plant for bamboo black liquor was set up using submerged bubble reactors. The SBR was supplied by Wagner-Biro (Austria) which developed such a reactor for gasification of water (Fig. 16). The plant was described by Judt (61), NKL - Celpap (12, 13) and Rajashekara (9). The salient features of the HNL plant (Fig. 17) are :

The design capacity of the plant is 40 m^3/h. It consists of three tanks each of 80 m^3 capacity and an operating level of 70 m^3. The first two tanks where pH is over 11 are of mild steel and the last tank, where the pH is around 10, is of stainless steel. The overflow from each tank goes to the next tank. In the first reactor tank there are two reactors followed by one reactor each in second and third tank. Although originally, it was planned to have two reactors in each tank, it was decided to have two reactors in the first tank and one reactor each in second and third tank, as the degree of carbonation, for initial neutralization of alkali, required in the first tank is relatively more compared to second and third tank receiving black liquors partially carbonated in first to second tank. Instead of six reactors, envisaged in the original design, only four reactors were planned due to limitation of UNIDO funds. The flue gas required for carbonation is drawn from chemical recovery furnace stack and connected to gas injection port located about 1.7 m below the reactor head. The rate of flue gas entering the reactor head is controlled by the dampers provided in flue gas line.

The combined foam formed in each tank, during carbonation, is taken to foam tank where the foam breaker converts the foam into black liquor. The black liquor collected at foam tank, is taken back to the first reactor tank.

The SBR reactor supplied by Wagner-Biro (Austria) is about 7 m high and U-shaped. The suction line which runs along the slope of reactor tank is connected to one end of the reactor through Oschner (propeller) circulation pump and flexible element. The other end of reactor is immersed in the tank. The gas injection port has a box with orifices of about 3 mm diameter and the gas enters the reactor head through these orifices at a right angle to the flow of black liquor. The gas liquor mixing takes place by way of circulation.

The carbonated black liquor, after attaining the desired end pH, is taken to hot retention tank of about 40 m^3 capacity. The hot retention facilitates the agglomeration of silica particles. After one hour hot retention, the liquor is taken to Delkor horizontal filter. The belt filter is a horizontal filter with a total filter area of about 9.6 m^2 (to handle about 40-50 m^3 of black liquor per hour). The wire fabric is supported by the moving belt with dams on the edges. The filtration takes place under vacuum provided by vacuum pump. The belt moves at slow speed, 1-4 rpm. There is a slight slope towards the liquor feeding end, so that the liquor sprayed from the headbox will have enough time to filter. Hot fresh water is used for washing the silica sludge and washing system is a counter current one, so that excessive dilution of black liquor is avoided. The mother filtrate from belt washer goes to realkalisation tank where the free alkali is raised by addition of caustic. Realkalised liquor is then taken to high pH for evaporation. The schematic lay-out of the desilication plant is shown on Fig. 17.

A horizontal belt vacuum filter is manufactured by Delkor, Germany and was installed for silica separation. The filter consists of a rubber transporter belt moving horizontally on HDPE (high density polyethylene) glide strips. The belt supports the filter cloth which is the filtering medium. There are grooves across the transporter belt to convey the filtrate to the centrally located holes and from there to the vacuum box positioned under the belt. From the vacuum box the filtrate air mixture goes to the filtrate receiver/air separator. The air is pulled by a vacuum pump and the filtrate flows down to the seal tank by a drop leg. The filter provides possibility to wash the silica in counter current mode. The filter cake is removed by a scraper from the filter cloth. The size of the filter is 9.6 m^2 which is expected to filter 40-50 m^3 of black liquor, corresponding to a 100 TPD pulp plant. The filter, being a drop leg type needs to be erected at high level (+10 m) which contributes to high building cost. The standard building cost is comparatively low in India and other developing countries.

One of the major advantages of this open type of filter earlier is its open design giving good accessibility. However, it also contributes to suction of air in the black liquor thus creating foam. The filter requires rather much space. Consequently, for bigger plants it might be justified to investigate other types of filters.

Operation experience :

The conditions of desilication were:

Total B.L. solids	14 -18 %
Temperature	65 -75 °C
pH	12.3-12.6 (at 30 °C)
SiO_2	3 - 6 g/l
Residual active alkali	5 - 8 g/l
Outlet from 1st tank pH	11.2-11.5 (at 30 °C)
Outlet from 2nd tank pH	10.5-10.8
Outlet from 3rd tank pH	10.0-10.2

The results of mill - scale desilication are presented in Table 29.

Table 29

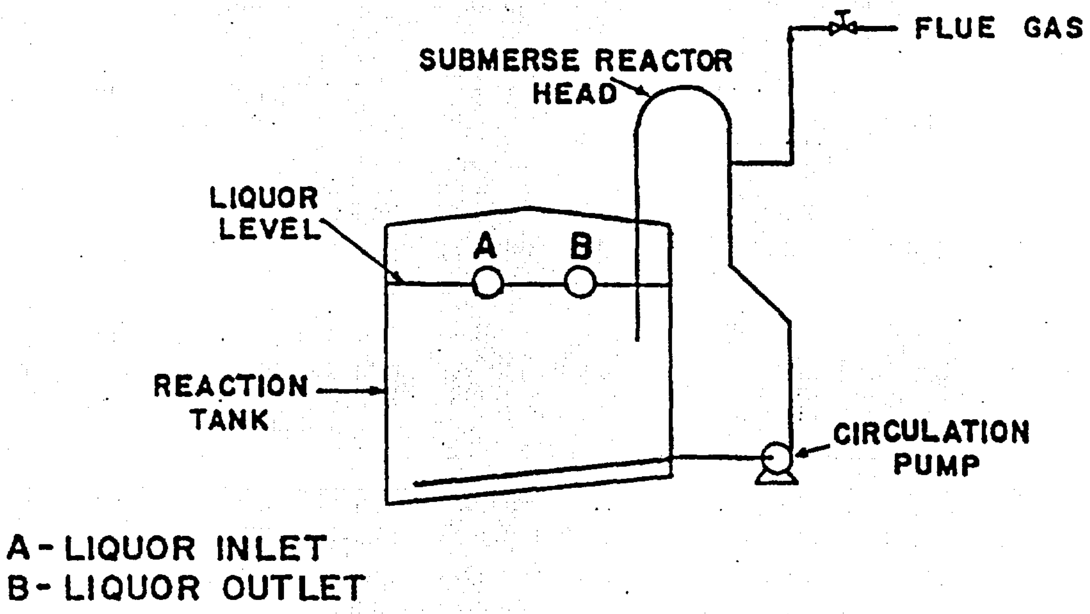
RESULTS OF DESILICATION ON PLANT SCALE *				
Parameters	Run Numbers			
	1	2	3	4
Feed liquor				
Total solids % w/w	20.9	17.0	17.6	16.4
RAA g/l as Na_2O	7.8	5.3	5.2	6.1
SiO_2 % w/w	2.83	2.60	1.80	2.36
pH at 30 °C	12.4	12.5	12.3	12.4
Filtration				
Feed m^3/hr	9	10	12	18
Temperature °C	62	65	68	66
Wash water m^3/hr	3.4	1.3	2.2	0.75
Belt speed m/min	3.5	3.0	3.0	4.0
Silica sludge **				
Moisture %	76.0	74.0	74.5	78.0
Ash at 600 °C	92.0	92.0	91.9	89.0
SiO_2 %	91.0	91.0	91.0	87.6
Lignin %	0.53	0.41	0.48	N.D.
Sodium %	2.5	1.8	2.4	N.D.
Desilication %	77.4	75.0	78.5	80.9

* Kraft black liquor from pulping of 80 % bamboo and 20 % reed.
**Expressed on o.d. sludge. Flue gas flow 400 m^3/hr having 8-10 % CO_2.
N.D. : Not determined

The main conclusions of the trials were :

- The carbonation with submerse bubble reactors is gentle and controlled. Considering low CO_2 content in flue gas about 50 m^3 of CO_2/m^3 of black liquor is required to bring down the pH of black liquor from 12.5 to 10.0. Foaming tendency with increased gas flow rates still continues to be a limitation for operating desilication plant at capacities higher than 10 m^2/h.

- Filtration of silica sludge on belt filter was highly satisfactory and black liquor up to 20 m^3/h has been filtered without problems. Filtration is sensitive to



SUBMERSED BUBBLE REACTOR
Fig 16
Source /6/

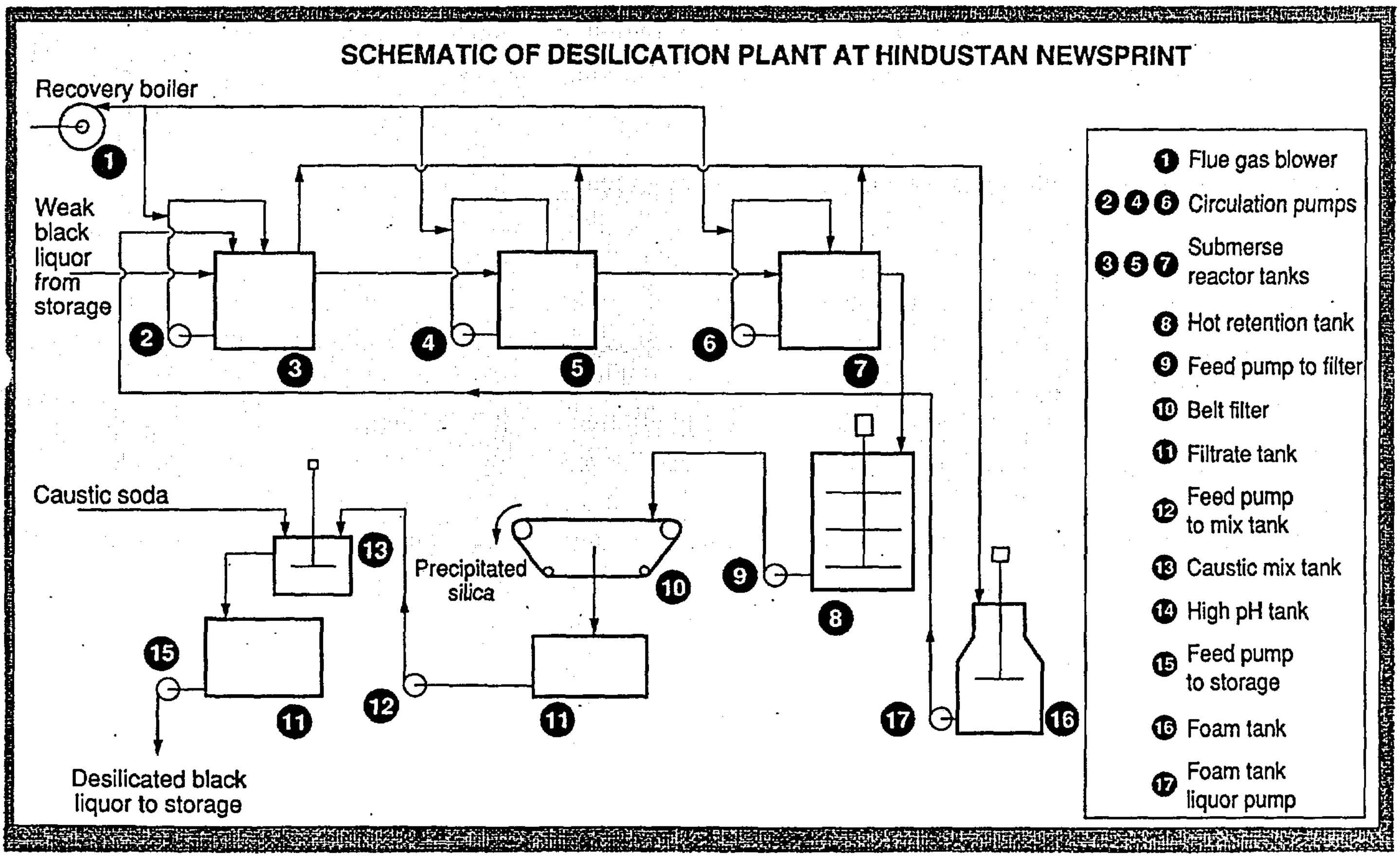

SCHEMATIC OF DESILICATION PLANT AT HINDUSTAN NEWSPRINT

Fig 17

temperature of carbonated black liquor and temperatures over 70 °C facilitates the efficient filtration. Filtration at lower temperature below 40 °C is difficult.

- There is a reduction of black liquor solids concentration after filtration by about 2 % and dilution to 11-16 %.
- The degree of desilication varied between 70-80 % and is closer to 80 % in most of the samples collected during continuous trials.
- The counter-current sludge washing was uniform and efficient as evident by high percentages of silica contents in the silica sludge and considerably low organic matter.
- Studies on decarbonation before realkalisation show that decarbonation is beneficial in reducing the alkali dosage during realkalisation stage. For instance to reach an optimum free alkali level of about 6 g/l as Na_2O, 9 kg/m^3 of alkali is required when the liquor is decarbonated while to reach the same free alkali level without decarbonation about 11 kg/m^3 of NaOH is required. In the plant scale the decarbonation is expected to be carried out after partial evaporation of the black liquor (intermediate effect of evaporator train) and then addition of alkali.

The plant is not in permanent operation, as less bamboo and more eucalypt is used and B.L. can be handled without desilication.

5.3.5 Other black liquor carbonation processes

Kraftanlagen Heidelberg of Munich (Germany) worked in late 1970's on a black liquor desilication process (65). Several CO_2 absorption equipment was tested but rejected such as absorption tower and Venturi injector. Finally a stream flow reactor was adopted. This consists of a number of connected tubes with Venturi type inserts mixing and partly disperging flue gas into black liquor under pressure. The flue gas is pressurized in a water-ring compressor. For silica sludge separation sedimentation, filtration on a drum filter and a decanter type centrifuge was tested but found as anappropriate. Finally a centrifuge of separator type was adopted. Desilication of rice straw black liquor was tested in a pilot plant in Rakta rice straw pulp mill (Egypt). Based on this experience an industrial scale desilication plant was supplied to PT. Kertas Leces mill (Indonesia) The results were disappointing. The plant is too complicated and some design features failed. The company stopped works in this field. Lurgi AG (Germany) developed a desilication process by carbonation, which was tested on pilot plant scale in the Rakta mill. Rice straw black liquor in the range of 8-15 % TDS is taken to a reaction tank after arresting its suspended matters. The liquor was subjected to a constant and vigorous agitation through a specially designed impeller located at the bottom of the tank.

A foam breaker was hooked up at the top of the reactor to suppress foam created during the process. Dustfree flue gas carrying 8-10 % of CO_2 from a boiler stack was fed into the reaction tank using a special compressor and a pressure of around 0.8 bar was maintained inside. Retention time was one hour, temperature at 60 °C. The undissolved CO_2 and excess air was discharged into the atmosphere. The liquor pH inside the reaction tank and of that going out was controlled by regulating the inflow of black liquor and/or flue gas into the reaction tank. The treated black liquor from the reactor was discharged into a deaeration tank and subsequently taken to a decanter. Most part of the precipitated material was separated in the decanter unit and partially clarified liquor is stored and further fed into a nozzle type centrifuge for second stage separation of precipitated matters.

Although Lurgi acknowledges the desilication system developed may be workable but expensive to operate and backed out on this issue.

A desilication process has been developed by the China Paper Industry Research Institute and tested in a 15 m^3/h W.B.L. pilot plant (10). The weak black liquor containing 6-8 g/l silica was treated by flue gas in a Venturi nozzle and pH lowered to pH 10.3 . The carbonated B.L. was clarified in a Dorr-Oliver type clarifier at 40-60 °C for 12 hours. The diluted sludge was separated on a separator centrifuge. The silica content in the clarified B.L. was 1-2 g/l, which is comparatively a low efficiency.

The CPPRI/UNIDO process when compared with the Kraftanlagen and Lurgi process is more simple. No high pressure flue gas is used. The carbonation in 3 stages is gentle, stepwise resulting in larger silica gel particles. A low speed, low head , high capacity axial flow pump is used preventing to high shear forces which may disintegrate gel particles. The belt filter is accessible, easy to clean and reliable in contrary to a separator centrifuge.

5.4 Green liquor desilication

Desilication of green liquor makes possible reburning of lime mud from causticizing. Accumulation of silica in black liquor and consequently scaling of black liquor evaporators will be reduced only if green liquor desilication is more effective than desilication in the causticizing process. However, even in this case, silica content in black liquor will be higher than after black liquor desilication.

5.4.1 Green liquor desilication by lime and alumina

Alumina is not effective in black liquor desilication. However when added to the smelt in the recovery furnace aluminium silicate is formed, which remains insoluble and can be removed with the dregs from the green liquor. This process is applied in a South African pulp mill.

Sodium silicate reacts with lime (see section 3.2.1 and 4.5). Mathur, Kulkarni e.g. (66) investigated a two-stage causticizing. In the first stage silica was precipitated by adding lime in a ratio silica to lime 1:1, 1:1.5 and 1:2. A 75 % desilication was achieved at a ratio 1:2 in laboratory scale (Table 30).

Table 30

ANALYSIS OF TWO STAGE CAUSTICIZATION (LABORATORY SCALE)

Particulars	1	2	3	4	5	6
Silica in green liquor, gpl	8.0	8.0	8.0	2.0	2.0	2.0
Silica : lime ratio	1:1	1:1.5	1:2	1:1	1:1.5	1:2
After Ist stage :						
Sludge generated/lt of green liquor, gms	23.0	28.0	34.0	5.0	5.5	6.5
Removal silica, %	52.5	64.4	75.4	57.5	65.0	75.0
Dryness, %	21.9	25.9	26.4	18.7	21.2	24.1
Silica in sludge, gms	4.2	5.2	6.0	1.1	1.3	1.5
After II stage						
Sodium hydroxide as Na_2O, gpl	67.5	69.3	73.1	69.1	73.4	75.4
Causticity, %	87.5	88.7	90.9	84.9	85.3	90.6
Causticization efficiency, %	85.0	87.6	88.8	81.2	84.3	90.6
Carbonate conversion, %	84.0	84.9	89.6	84.0	88.7	94.4
Sludge generated/lt of green liquor, gms	95.0	92.0	90.0	104.0	101.0	95.0
Dryness, %	36.6	39.2	44.1	39.7	44.5	49.8
Silica in sludge, %	3.5	3.2	2.2	0.8	0.7	0.5

Source (66)

Evidently a 1:2 silica to lime ratio is required to obtain 75 % desilication. The amount of high silica containing sludge (18-22 % silica) is about 3-4 times the weight of silica in green liquor (on O.D. basis).

In the second stage of causticization, the desilicated green liquor is causticized in the conventional way. As the major portion of silica has already been removed in the first stage, the lime sludge generated in the second stage of causticization contains small amounts of silica which is well within the limits and can be reburnt without any problems The results recorded in Table 30 indicate that even with 8 gpl silica in green liquor about 75 % desilication is possible and the resulting green liquor can be causticized in the second stage with high degree of causticity & better settling of lime mud. However according Mathur and Kulkarni (66) desilication is effective at a temperature of 60 °C and the green liquor has to be cooled and afterwards reheated to 90 °C prior to 2nd stage causticizing. This would require steam and the danger of heat exchanger fouling is high.

Win Sin (3) reported about successful desilication of bamboo kraft liquor by two stage causticizing even at a temperature 90 °C at 30-60 min retention time. The process was tested in pilot continuous operation with desilication efficiency 75±10 % at a silica : lime ratio 1.5 to 2.0 .The equipment for desilication by pre-causticizing is the same as for causticizing : a pre-slaker, pre-causticizer and green liquor clarifier, which could be the same as for causticizing the sludge containing silica could be processed together with causticizing dregs and washed in two stages in a sedimentation type washer.

Green liquor desilication is in operation in the Italian Foggia mill (22). Milk of lime is added to the dissolving tank in such amount, that about 3 % of Na_2CO_3 is causticized to NaOH. The calcium silicate is separated by sedimentation and dewatered to 50 % DS by a filter press. The amount of O.D. sludge is about 100 kg per ton of unbleached pulp. In Foggia there is no second stage causticizing and the desilicated green liquor is used in the NACO pulping process (22).

5.4.2 Green liquor desilication by carbonation

The already mill-tested carbonation has been investigated by Mathur and Kulkarni (66) for desilication of green liquor using flue gases from lime kiln to final pH value 9.5 at a temperature above 90 °C. The efficiency was about 90 %. A cleen, white SiO_2 was formed. Sodium carbonate is converted to bicarbonate which may cause difficulties in separation of lime mud by settling. Bicarbonate can be converted to carbonate by steam stripping. The advantage of green liquor desilication by carbonation is absence of lignin which may partly co-precipitate in desilication of black liquor. Silica built-up is depressed, but silica concentration in black liquor is higher when desilicating green liquor. In black liquor desilication the silica dissolved from fibrous raw material is to large extent separated and does not enter evaporators. Green liquor desilication is a part of the MKCR process (see chapter 6) using CO_2 from lime kiln, which is first absorbed in monoethanolamine and desorbed to get high concentration CO_2.

5.5 Technical and cost-benefit evaluation of desilication processes

5.5.1 Technical evaluation

Silica has a negative impact on both the alkali circulation systems (evaporation - - incineration - causticizing) and lime circulation system (lime mud settling in white liquor clarification - lime mud washing and dewatering - lime reburning). The impact of a desilication process has to be evaluated in both systems. Raw material cleaning has a positive impact on both systems, but the efficiency is low (max. 50 %).

Black liquor desilication has a positive impact on both circulation systems. The residual silica content in carbonation desilication is limited by the solubility of silica at the each pH of the desilication process. Consequently, the higher the silica content in the B.L., the higher the desilication efficiency, but the end effect is practically the same. The desilication efficiency achieved in semi-industrial scale was 80-90 %.

Green liquor desilication has actually a positive impact on the lime circulation system only, i.e. it makes possible lime reburning even at a high silica content in black liquor, but does not reduces e.g. scaling in evaporators. A slight positive impact on the alkali circulation system could be in case the green liquor desilication process has a higher desilication efficiency, than the causticizing process, which is also a desilication process. This could be in case of green liquor desilication by the carbonation process, which might have a higher efficiency than the black liquor carbonatisation process as in absence of lignin in green liquor carbonatisation can be carried out to a lower pH, i.e. lower silica solubility.

Desilication of black liquor makes possible lime mud reburning and, consequently purchased lime saving. In addition to this the following benefits can be expected in the alkali circulation system.

- Less plugging of washer wire meshes.
- Improved steam economy in evaporation of black liquor . According Kulkarni and Pant (64) steam economy may increase by 0.5 to 1.0 tonnes of evaporated water per ton of steam. However, it is difficult to present exact data as comparative mill or pilot scale evaporation with desilicated and no-desilicated B.L. are not available. By comparison of mill data pertaining non-desilicated non-wood B.L. evaporation with wood B.L. evaporation similar data can be calculated (see section 4.3.8). In these evaluation we calculate improvement of steam economy 0.7 .
- Decrease of sodium hydroxide losses in lime mud (2 % on A.A. charge i.e. about 6 kg/t of pulp).
- Reduced shut-down of chemical recovery. It is anticipated, that compensation of this shut-down time requires increase of chemical recovery capacity by 15%. However increase of investment cost is not linear due to economy of scale. It we apply for this increase of capacity the "one-sixth" rule, than the increase of investment cost is 8.7 %. Taking into account other expenses such as larger tanks for medium-concentrated black liquor for storing during shut-down of recovery we may calculate 10 % investment cost increase without desilication, or 10 % reduced investment cost if considering desilication.
- An additional benefit is marketing of the isolated silica, which can be potentially used in various industries such as rubber, pharmaceutical, tyre, electronic, paint etc. The estimated price in 1993 was INR 15/kg (64).

The benefits of green liquor desilication are saving of lime (quicklime). The cost-benefit calculation of both alternatives has to be based on a complete desilication - lime reburning system.

5.5.2 Cost-benefit calculation

The prices of chemical and energy are listed in Chapter 7. The investment cost for desilication plant for a 160 TPD pulp mill have been estimated in 1991 by NLK-CELPAP to INR 14 million (12, 13). In 1988 and 1993 CPPRI estimated investment cost for desilication for a 50 and 100 TPD mill to INR 20 million. Both estimates are too low. The budgetary prices indicated in IV. Quarter 1995 by Enmas Process Technologies (licensees of the UNIDO-CPPRI desilication process) are as follows

B.L. dry solids capacity TPD		70	160	300
Design, manufacture and supply	INR million	68	92	120
Erection and commissioning	INR million	2.5	3.5	4.5
Total cost (approx)	INR million	70.5	95.5	124.5

Note : Desilication efficiency 85-90 %
Power : 2-2.5 kW/m^3 B.L. (considered too low by the author)
This will increase investment cost for recovery of chemicals by 25-30 %.

The operating cost-benefit calculation with realistic investment cost and chemicals and energy costs as in IV. Quarter 1995 (see Chapter 7) is based on material and energy data of NLK-CELPAP (12, 13) and is presented in several alternatives :

Alternative "A" takes into account all cost and as benefit recovery of lime and reduced caustic soda loss in lime mud after desilication (losses without desilication are higher by 2 % NaOH on pulp).
Alternative "B" includes saving of steam in B.L. evaporation after desilication (improvement of steam economy from 3.2 to 4.2 see Table 23). Such an improvement of steam economy, if any, is realistic with straw B.L. only, and should be investigated by detailed analysis of mills.
Steam economy in bagasse B.L. evaporation should be about 4 in modern evaporators.
Alternative "C" includes in addition benefits from marketing of isolated silica, about INR 12-15/kg, i.e. about 20-25 kg/t of pulp (INR 300/t of pulp).

Regarding capital cost two alternatives are considered :

Alternative 1 (basic alternative) :Capital cost include lime reburning kiln and desilication process equipment depreciation (12 %) and 15 % interest rate (total 27 %).
Alternative 2 includes 10 % lower investment cost for chemical recovery due to less down-time in recovery after desilication. This is hypothetical value and likely only with straw B.L. This should be verified by detailed, long-term analysis of mills.

The investment cost of desilication for 216 TPD dry solids can be calculated from the above mentioned capacities by the equation :

Cost of equipment capacity a = cost of equip. cap. b (capac. a / capac. b)$^{0.6}$

Table 31

OPERATING COST AND BENEFITS OF LIME SLUDGE REBURNING AND DESILICATION (160 TPD mill, 216 TPD dry solids)

ALTERNATIVE "A"	Case I. with desilication and lime reburning	Case II. without desilication and lime reburning
Burnt lime requirement (100 %) TPD for causticizing	40	40
Available CaO %	80	70
Actual requirement TPD	50	57
Make-up lime TPD	-	57
Make-up limestone TPD	8	-
Unit cost of make-up INR/t (including transport cost)	1,850 (limestone)	3,250 (quick lime)
Make-up cost INR/d	**14,800**	**185,250**
Fuel oil requirement kg/t lime	205	-
Fuel oil cost INR/t	6,000	-
Fuel oil cost INR/d (0.205x50x6,000)	**61,500**	-
Power, labour, maintenance INR/d	**5,850**	-
Steam cost INR/d	**21,600**	-
Sludge disposal cost INR/d	**570**	**5,700**
Steam for desilication TPD (0.3 t/t pulp)	48	-
Increased caustic soda loss t/d (2% on pulp)	-	3.2
Cost of extra make-up caustic soda (INR 14,000/t)	-	**44,800**
White liquor for realkalisation TPD (40 kg/t of pulp, 4 INR/kg)	6.4	-
Cost of white liquor INR/d	**25,600**	-
Total operating cost INR/d	**129,920**	**235,750**
Operating cost INR/t pulp	*812*	*1,473*
ALTERNATIVE "B" - increased steam requirement for B.L. evaporation (1.71 GJ/t DS)		**93,957**
Total operating cost INR/d	**129,920**	**329,707**
Total operating cost INR/t pulp	*812*	*2,060*

Total investment for		17,150 TPA pulp	55,000 TPA pulp
Lime sludge reburning	INR million	29.8	46.8
Desilication	INR million	70.5	107.6
Total	INR million	100.3	154.4
Capital cost 27 %	INR million/a	27.08	41.68
Capital cost	INR / t pulp	1,759	756

Operation of recovery system without desilication may result in increased down-time due to cleaning. On the other side desilication reduces down-time. To compensate increased down-time capacity of the recovery system has to be increased by about 10 % and on the contrary if desilication is applied the capacity can be reduced by 10 %. This reduction results in decreased capital cost as shown in next table :

		Capacity of pulp TPA	
		17,150	55,000
Reduced investment	INR million	14.18	25.7
Reduced capital cost	INR million	3.82	6.34
Reduced capital cost	INR /t of pulp	222	115

Total cost of lime sludge reburning and desilication

		I. Mill capacity 17,500 TPA	II. Mill capacity 55,000 TPA
Operating cost	INR /t of pulp	812	812
Capital cost	INR /t of pulp	1,759	756
Total cost	INR /t of pulp	2,571	1,568

Savings INR /t (Difference between total cost and operating cost without desilication)

	I.	II.	Pay-back period years (for II.)
Alternative A/1 (basic alternative)	- 1,098	- 95	(losses)
Alternative B/1 (improved steam economy)	- 511	+ 492	5.7
Alternative B/2 (B/1 plus reduced investment)	- 289	+ 607	4.62
Alternative C (B/2 plus marketing silica)	+ 11	+ 907	3.01

Green liquor desilication by two-stage causticizing is more simple. The investment cost for a 50 TPD (17,150 TPA) mill may be around INR 15 mil, i.e. at 27 % capital cost the capital cost per ton of pulp INR 236 . Operating cost item 7 increased by 20%, item 13 by 100 %, item 11 reduced by 30 % are totaling INR 552/t. Total cost INR 788/t of pulp resulting in a pay-back period of 1.3 year. However, this makes only possible to reburn lime, but no improvement in recovery. The process is still not established.

5.5.3 Conclusions

Earlier cost-benefit evaluation of the carbonation desilication process presumed considerably lower investment cost. Quoted investment cost (by licensee) are 3 times higher that the investment cost estimated by NLK-CELPAP (12, 13) and two times higher, if we calculate NLK-CELPAP estimate plus 40 % inflation against 1991. Even with the low investment cost NLK-CELPAP indicated, that lime reburning in combination with desilication does not bring savings, cost of reburned lime is higher, that of purchased lime. Kulkarni and Pant (64) included into benefits of desilication improved steam economy in evaporation, reduced down-time and marketing (selling) of isolated silica. Incorporating these benefits a positive economy could be identified with pay-back periods as low as 3 years. However, this may be valid for a capacity 160 TPD pulp (55,000 TPA). When considering a small pulp mill of 50 TPD capacity (17,150 TPA) there are no savings with desilication. The process is strongly dependent on economy of scale.

It is also mentioned, that the benefits of higher steam economy in evaporation and reduced down-time are hypothetical and should be confirmed in mill scale or by testing evaporation on pilot scale under controlled conditions.

Application of desilication may be necessary irrespective of savings if the black liquor can not be processed in recovery without desilication. This may be the case of rice black liquor recovery.

Another alternative may be application of modified evaporators, which are less sensitive to scaling.

5.5.4 Recommendations

- In contact with manufacturing companies explore possibility to reduce investment cost of the black liquor carbonation process.
- To investigate possibilities to improve desilication efficiency by chemical aids (floculating agents).
- To explore marketing of silica.
- In case of industrial application to test improvement of evaporation steam economy.
- To investigate more in detail desilication of white liquor by two-stage causticizing in order to improve desilication efficiency.

6. UNCONVENTIONAL AND EMERGING RECOVERY PROCESSES

6.1 Recovery processes commercially operated on wood black liquor

6.1.1 Wet air oxidation of weak black liquor (WAO)

The WAO process is an oxidation of dissolved or dispersed organic material with molecular oxygen at elevated pressure and temperature. It was a longer time used for oxidation of sludges (ZIMPRO process). For oxidation of cooking black liquor a temperature 320-325 °C and a residence time of about 100 minutes is required to obtain a level of 95 to 98 oxidation which is required to recover the inorganic chemicals. A typical pressure is 20 MPa. The WAO process is used in the Australian Burnie mill for recovery from eucalyptus soda black liquor (67, 68). The oxidizing reaction has two phases. In the first, fast phase 90 % of the organic material is oxidized to short chain aliphatic compounds such as sodium acetate and carbon dioxide. This requires about 25 % of the reactor volume. In the second, slow phase the sodium acetate is oxidized to carbon dioxide. The oxidizing reactions are exothermic and the heat is removed by converting a part of water to steam. The concentration of the black liquor entering the reactor and the amount of evaporated water from the reactor is limited by the concentration of sodium carbonate and bicarbonate generated by oxidation of organic matter. This should not be higher than 110 g/l (as NaOH) to prevent carbonate precipitation as sodium carbonate shows inverse solubility at high temperature. The feed to the reactor can be as low as 8 % total solids, but 12 to 16 % is preferred for greater thermal efficiency. At the higher concentrations the feed is diluted by condensate of flash steam used for process steam preparation. The oxidized liquor concentrated to 180 g/l by flashing to atmospheric pressure contains sodium carbonate and bicarbonate (75:25) and sodium salts of short chain aliphatic acids such as sodium acetate equivalent to 95-98 % oxidation sodium acetate is recycled with the liquor and does not interfere with cooking or causticizing if oxidation is at least 94 %. The oxidized liquor contains no carbon particles. Dregs of the liquor containing a substantial part of inorganic impurities are settled and removed prior to causticizing. Most of the aluminium, about 70 % of calcium and 50-70 % silica are removed at this stage, as pH after oxidation is pH 8.5-9.0 . The oxidized liquor is causticized in a conventional process. Care must be taken to avoid excessive dilution of white liquor as the concentration of oxidized liquor is lower, than concentration of dissolved smelt from recovery boiler.

In the Burnie mill eucalypt cold soda black liquor is oxidized (Fig. 18) The first WAO plant was handling black liquor from 30 t/day. Since 1979 a new plant for 90 t/day pulp is in operation. Atmospheric air is filtered and compressed to about 1.3 MPa by a three stage centrifugal compressor (3,400 kW motor) and to 21 MPa by a three stage reciprocating compressor driven by a 3,500 kW motor. Output is 31,000 kg/h of dry air at 150 °C. Spent black liquor from the digesters is diluted with water heated with flash steam and pumped to the reactor by a five plunger high pressure pumps and mixed with return condensate. The air and black liquor flow is co-current. Oxidized liquor is flashed in two stages. Steam is produced for heating of B.L. and for production of 2.5 MPa process steam in reheaters. About 35 t/h process steam is produced (about 9 t/t of pulp). The chemical recovery efficiency is about 99 %. The thermal efficiency calculated as available water vapour in GJ/h against input enthalpy GJ/h is about 75 %. However electric energy consumption is about ten times higher than in an evaporator-recovery boiler system. Some of the energy may be recovered as achieved in commercial scale in waste (sludge) oxidation (68).

Initially there have been several material, installation and design faults but these have been eliminated and the uptime is exceeding 93 %. Scaling has been also a problem. Pre-heating of diluted black liquor with oxidized black liquor in a heat exchanger resulted in heavy scaling and has been replaced by flash vapour heating. The main scale elements were calcium, aluminium, silica and magnesium. This was overcome by process changes in causticizing and clarification of oxidized liquor as well as by duplication of the oxidized liquor system.

The capital costs of the WAO recovery system have been in Burnie mill significantly higher than the cost of an evaporator-smelt boiler unit of the same capacity. A WAO system was installed to process black liquor from 400 t/day of semichemical pulp production in 1975 in the Champion International, Ontonagon, Michigan, USA mill. It seems, recently some possibilities were found to reduce capital costs as a WAO system is in the final round of selection for a hemp-sisal project in Spain.

WAO of bagasse black liquor was tested in laboratory scale with good results. Desilication was about 70 %. Pith was also added in some experiments.

Advantages of the WAO system from agro-based black liquor recovery point of view is the absence of black liquor evaporation, i.e. no problem with high black liquor viscosity and silica scaling of evaporators.

Disadvantage is the high capital cost and high electric energy consumption. This is a problem in India where mills depend on public grid and suffer from power shedding. This may be detrimental for the WAO process. It is noted that the WAO process is a high-tech process comparable with ammonia synthesis.
Obviously more development work is required as follows :

- Testing of WAO with oxygen enriched air. This may reduce necessary pressure, reducing electrical energy demand and reactor volume.
- Testing of silica settling and filtrability after oxidizing especially rice straw black liquor by comparison with silica properties from carbonation.
- Detailed engineering calculations of possibility of el. energy recovery and co-generation from flash vapour or process steam.
- Testing of possibility of contra-current flow of air and B.L. in the reactor in order to improve oxidation of sodium acetate.

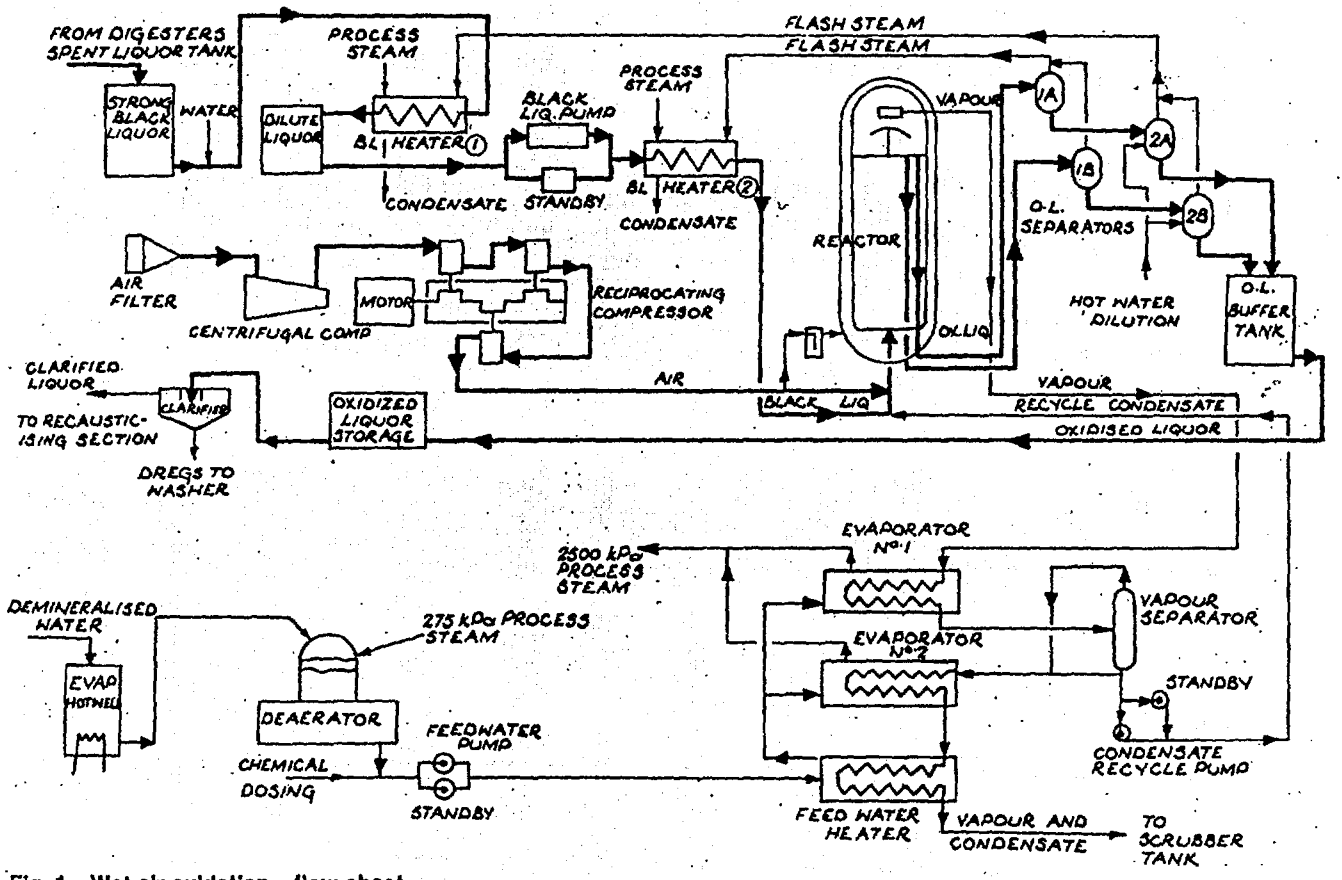


Fig. 1—Wet air oxidation—flow sheet

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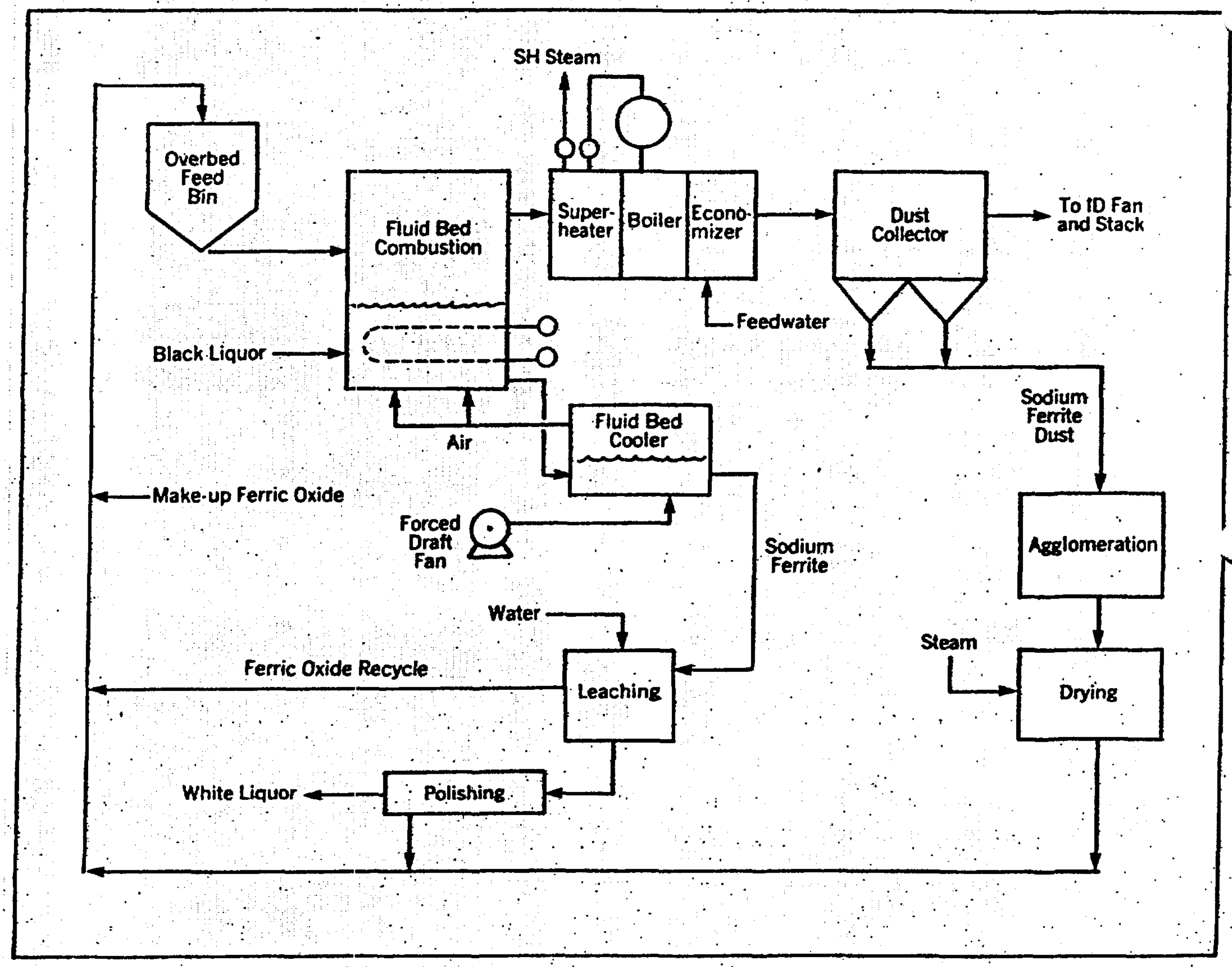
WET AIR OXIDATION OF BLACK LIQUOR
Fig 18

Source /68/



Direct Alkali System Process Schematic

DIRECT ALKALI RECOVERY PROCESS /DARS/
Fig 19

Source /1/

6.1.2 Direct alkali recovery system (DARS)

This system is based on the long time known reaction of ferric oxide with sodium carbonate forming sodium ferrite

$$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2 \qquad [1]$$

and on the reaction of sodium ferrite with water

$$Na_2Fe_2O_4 + H_2O = 2\ NaOH + Fe_2O_3 \qquad [2]$$

These reactions make it possible to recover sodium hydroxide without causticizing of sodium carbonate. Only black liquors not containing sulphur are suitable i.e. only soda pulping B.L. A suitable industrial process using this reaction using fluid bed incinerator has been developed by Toyo Pulp Japan and Australian Paper Manufacturers (APM) (69). Toyo and APM licensed this process to Babcock and Wilcox, but at the present time no company is marketing this process. After testing in an APM pilot plant the DARS process has been installed in the Burnie mill of Australian paper. After eliminating several teething problems the DARS process in Burnie is in full commercial operation recovering chemicals from soda-anthraquinone pulping of mixed hardwoods, predominantly eucalypts. A second commercial installation for wheat straw soda black liquor was in the Fredericia mill (70) in Denmark but operation was discontinued due to several operation problems. Agricultural residues B.L. recovery was tested in the framework of an UNIDO assisted project in the Central Pulp and Paper Research Institute in Saharanpur (India) (73, 74). The DARS process has been described in several publications (69-72)(4, 5).

In the process shown in Fig. 19 black liquor from soda pulping is burned with particles (1-3 mm) of hematite (Fe_2O_3) in a fluid bed incinerator. Acceptable firing concentrations can be as low as 40 % dry solids, with higher levels requiring deployment of boiler or superheater tubes in the bed for excess heat removal. Low concentration of B.L. is an advantage of the process as scaling of evaporators when evaporating agro-based B.L. increases significantly at concentrations over 35-40 %.

When introduced to the hot bed material, the black liquor organics (mainly lignin) are burned producing CO_2 and H_2O. Sodium attached to the lignin molecules is oxidized to Na_2O which in the CO_2 - containing atmosphere is unstable and forms Na_2CO_3. The presence of Fe_2O_3 catalyzes thermal decomposition of black liquor at relatively low temperature and furthermore catalyzes decomposition of Na_2CO_3 to CO_2 and Na_2O, the Na_2O reacting with Fe_2O_3 producing $NaFeO_2$. Below 851 °C the reaction is of solid-solid nature and fairly slow. At 851 °C the sodium carbonate melts so the reaction turns to a solid-liquid nature and therefore faster. Reaction rate increases up to 900 °C, but not significantly above this temperature. With residence time in the reactor of 1-2 hours at 900 °C, the reaction will generally be completed approx. 95 % if there remains sufficient free iron oxide in the bed. At lowering the amount of free iron oxide the availability of iron oxide for reaction reduces and causticity (expression for how many percentage of

Na_2CO_3 has turned into $NaFeO_2$) can decrease. At 900 °C causticity will not be significantly affected, if more than one third of the total Fe_2O_3 is free. At lowering excess iron below this, a decrease in causticity is observed, but, causticity of 90 % can be achieved with only one tenth of total Fe_2O_3 free for reaction. If all Fe_2O_3 has been turned into sodium ferrite and additional black liquor is supplied, the Na_2CO_3 formed can not react and will remain as a melted phase. An increasing content of melted Na_2CO_3 sticking between particles increases and can eventually lead to defluidization in the reactor.

Flue gases containing entrained dust (mainly sodium ferrite) are cleaned in a suitable gas clean up device (usually multicyclones and a wet scrubber).

The solid bed product, consisting mainly of sodium ferrite and unreacted ferric oxide is cooled in a fluidized bed cooler which acts also as fluidization air preheater.

The cooled sodium ferrite is hydrolyzed at 90-100 °C according reaction [2], which is exothermic and no additional heat is required to maintain desired temperature. Leaching at a lower temperature has no deleterious effect beyond reducing leaching efficiency. The system is capable of producing white liquor up to 94 % causticity and 300 g/l NaOH concentration.

The application of the DARS process for non-wood especially bagasse, wheat and rice straw black liquor recovery was investigated by CPPRI in laboratory and pilot plant scale (4, 5, 74). The pilot plant refractory lined fluid bed reactor has a diameter of 900 mm, total height 3,500 mm. The reactor was designed for incineration of 275 kg/h B.L. solids. The reactor was operated batch-wise using 0.9 mm ferric oxide particles. The leacher is a vertical column (volume 180 litres, total height 4,175 mm) working in a counter current operation with sodium ferrite introduced on the top and leaching water at the bottom of the column.

The DARS process was installed in the Danish Fredericia wheat straw pulp mill (70). The capacity of the mill was 150 BDMT/day of pulp. The recovery was designed for 19 t/h strong black liquor (46 % TDS). The B.L. was evaporated on falling film evaporators (5 bodies, 4 effects) with a total heating surface 715 m^2. The inlet concentration of B.L. was 12 %. Due to good cleaning of straw the silica content in black liquor was 1 % only. The reactor surface area was 18 m^2. The reactor was connected with a steam boiler. The recovery could not be operated properly and continuously due to failure of some equipment and operation difficulties. Marketing problems contributed to closing of the mill.

The experience from laboratory research, from the pilot plant experiments and from operation of the Fredericia mill regarding process difficulties and straw black liquor processing can be summarized as follows :

Grinded iron ore and pelletized iron ore dust were used. Grinded iron ore has a higher density, is less porous, has lesser sodium binding capacity and requires more fluidization air. Dust formation is comparatively low. Danish pelletized ore was more easy to fluidize, has a higher binding capacity but generates high amount of dust (about 25 %).

Non-process elements are tolerated to greater extent in the DARS process than in a conventional recovery boiler. Potassium carbonate is bound to potassium ferrite and hydrolysed to KOH, which is a cooking chemical as NaOH. Sodium sulphate - if present - and sodium chloride does not effect the DARS process directly.

Sulphate most probably exists as melted phase and accumulation of sulphate may lead to sticking of particles to lumps and defluidisation. A part of sulphate leaves the reactor with dust. Chlorides sublimate at 900 °C and upon cooling of flue gases condense on dust particles. Sulphates and chlorides can be removed from the dust by washing with cold water and hydrolysis of sodium ferrite with cold water is limited, but some losses will occur. It may be necessary to wash a part of the cooled bed material as well.

Sodium silicate is bound structurally to ferrite (5). The nature of silicate in the ferrite is still not know, it has no appreciable influence on causticity in the reactor (provided excess ferric oxide is available), but decreases significantly hydrolysis. Sodium and silica accumulation (73) during batch experiments in the fluid bed reactor is shown in the following Table :

Table 31

SODIUM & SILICA BUILD-UP DURING RECYCLING OF ORE IN DARS

	Ore			Ore	
	A**			B**	
	1st	2nd	3rd	1st	2nd
Sodium as Na_2O*, %	6.3	8.1	8.4	7.8	8.2
Silica as SiO_2, %	3.5	6.3	8.4	6.3	9.8

* Initial ores showed no sodium content

** Recovered Fe_2O_3 (ores) recycled in subsequent cycles

A, B different Indian ores

Accumulation of silica may be also influenced by NaOH concentration in the leacher as with increasing NaOH concentration SiO_2 concentration in white liquor increases. Calcium also forms an insoluble compound with Fe_2O_3. Obviously when incinerating silica containing black liquors a considerable part of bed material (hydrolysed ferric oxide) has to be purged which will also increase sodium losses. It can be speculated, that silica accumulation in the bed material (Fe_2O_3) will result in such a decrease of binding capacity, that a part of sodium carbonate will remain melted resulting in sticking of particles, lump formation and eventually in defluidization.

Some problems in Fredericia mill can be listed as follows :

- The bed material were pellets formed from dust. The pellets quickly disintegrated in the reactor may be due to the fact, that the pellets were wet (not dried).
- Excessive dust plugged economizer part of the boiler.
- The dust had shorter residence time as pellets and reacted only partly with black liquor.
- The dust resulted in blockage of leacher inlet and outlet, compressed dust blocked screen conveyor and caused channeling in the column. Filters were overloaded.

- In the fluid bed hard lumps were formed resulting in defluidization. Reasons for hard lumps formation may have been a reductive atmosphere resulting in magnetite formation and melted phase iron compounds reducing porosity of particles and permeability to oxygen. Accumulated silica may also caused problems.
- Abrasion of moving parts of leacher by dust. The leacher should not have moving parts.
- Pellet preparing by tumbling in a mixer was leading to pellets of low mechanical strength.

Due to bad market and consequently critical financial situation Fredericia was closed. The Burnie mill was closed temporarily but after reconstruction and modifying the DARS recovery is working smoothly (75).

It seems, that the further development of the DARS process has to be based on experience of Burnie mill, but additional investigations may be required to adopt this process to non-wood fibres containing silica. Reliable data can be obtained in a continuously operating plant or pilot plant. It is suggested to upgrade the DARS pilot of CPPRI to continuous operation. However, it may be useful to transfer the pilot plant equipment to an agro-based mill.

Once the operational problems are solved the DARS process may have the following advantage :

- No need of highly concentrated black liquor - less problem with evaporator scaling.
- Simple scaling down to low capacity.
- No need of causticizing with lime, no lime mud problems, no lime mud reburning, no high-grade fuel for causticizing.
- Lower investment costs by about 20-25 %.
- Possibility of further simplification - no steam boiler, lower B.L. concentration - simple 2-3 effect evaporator - direct contact evaporator.
- No smelt, no explosion danger.

Recovery efficiency can not be estimated, as this will depend on necessity of purging leached sodium ferrite bed material or dust, which still will contain sodium.

At present time there is not sufficient experience with application of the DARS process for non-wood black liquors.

In Japan (76) a water-wall cooled bubbling type fluid bed incinerator-reactor was tested in pilot plant scale. The ferric oxide pellets were prepared by compacting. Black liquor of 80 % concentration was over-bed sprayed using a rotating spray nozzle. Incineration temperature was over 900 °C. About 65 % sodium was recovered from overflow granules (pellets) and 35 % from flue gas dust. The optimum sodium and water contents of the pellet iron oxide should be 6 % and 9 % respectively. According a feasibility study the investment cost are 6.7 % lower than for a conventional recovery, even if the fluid bed recovery boiler is more expensive than a conventional one. This type of direct causticizing process seems to be too complicated for a small agro-based mill.

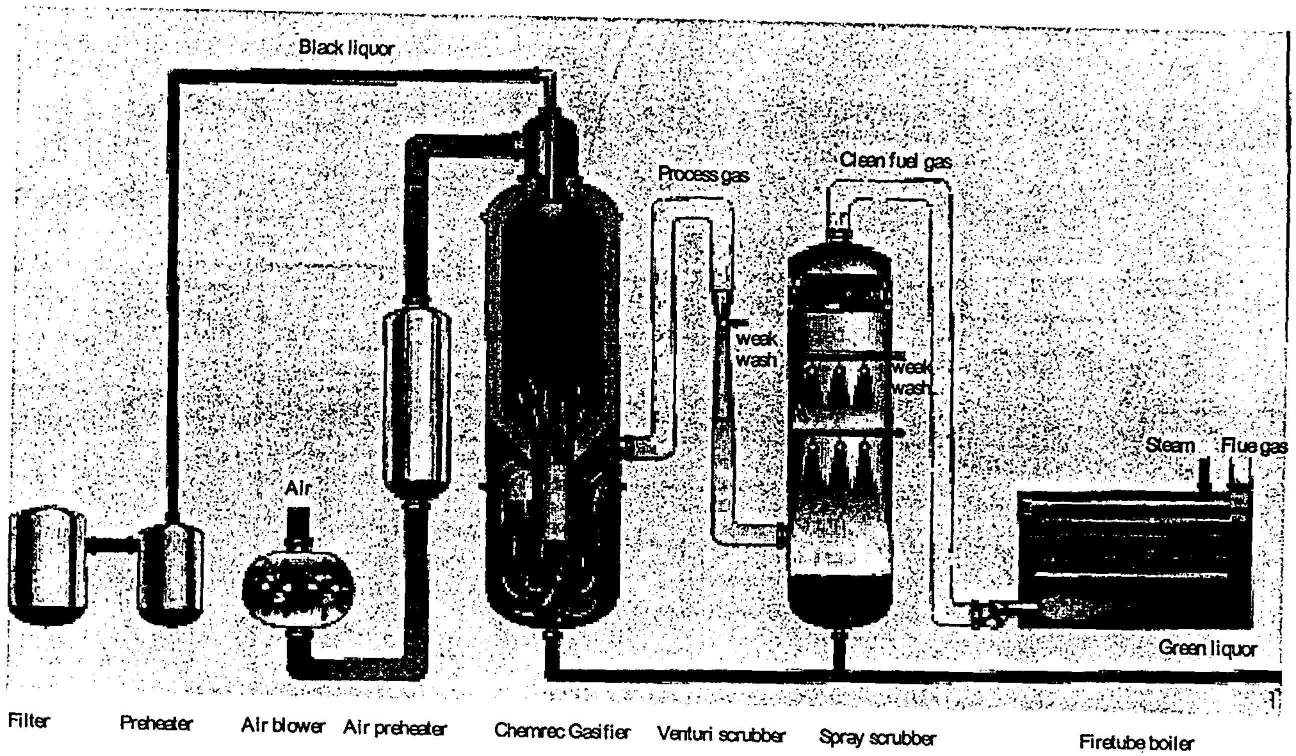


Fig.20
CHEMREC BLACK LIQUOR GASIFICATION SYSTEM
Source /77/

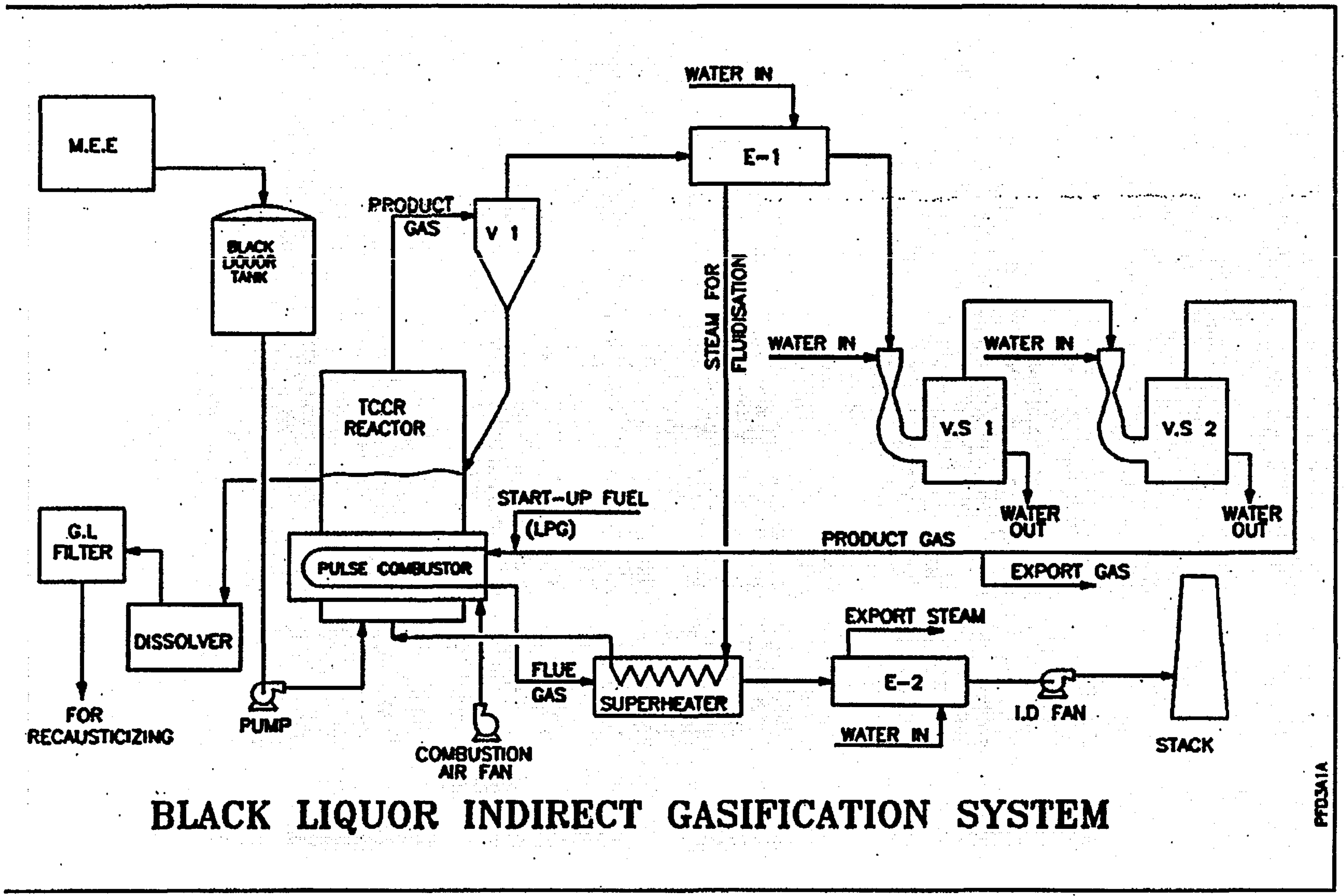


Fig.21
MTCI - ESVIN GASIFICATION SYSTEM
Source /78, 79/

6.1.3 Direct gasification of black liquor by the CHEMREC system

Gasification of black liquor instead of direct incineration is pursued by several companies (77). The first commercially operated system in the CHEMREC system (Kvaerner Group) installed in the Assi Domän Frővitors Mill in Sweden. It is used as a booster increasing the capacity of the recovery system. The capacity of the CHEMREC booster is 72 tonnes dry solids per day corresponding to about 15000 tonnes of pulp per year.

The core of the CHEMREC system (Fig. 20) is the gasifier, a refractory lined entrained bed reactor where concentrated black liquor is gasified under reducing conditions using preheated air. Kraft black liquor is fed to the gasifier in spray form, together with preheated air. The gas mixture that is formed at around 950 °C contains carbon monoxide and hydrogen as well as molten sodium salts in the form of fine droplets. The smelt droplets and the combustible gas are separated in a quench dissolver where they are brought into direct contact with aqueous cooling liquid. The droplets dissolve to green liquor. The gas leaving the quench dissolver is scrubbed in a separate scrubber to remove residual hydrogen sulphide. Cleaning of unburned gas has the advantage, that the gas has less than half of the volume of the corresponding flue gases. The cleaned gas is combusted in an existing boiler or in a package boiler. The CHEMREC process is an outgrowth of plasma technology. Direct conversion of black liquor to white liquor by plasma technology is in principle possible but consumes for too much electricity to be of commercial interest. In the present form of the CHEMREC process plasma technology has a subordinate role. A plasma generator is installed, but preheating of the air entering the gasifier could be done in another way e.g. by burning the combustible gases generated by the process itself. The CHEMREC process promises electrical power yield of about 25 % instead of about 13 % in the conventional soda recovery boiler. The CHEMREC gasifier can process other spent liquors e.g. spent liquor from oxygen delignification and obviously from soda pulping as well.

6.2 Emerging recovery processes

In this section new recovery processes are discussed tested on laboratory bench scale or pilot plant scale and are considered as promising.

6.2.1 Indirect gasification of black liquor

The MTCI system is indirectly gasifying black liquor in the pulse assisted TCCR (ThermoChemical Conversion Reactor) which the heart of the system (78, 79). The pulsation results in velocity fluctuations in the resonant fire tubes. The gasifier comprises a steam fluidized bed containing an array of immersed heat transfer tubes (fire tubes) (Fig. 21). The pulsation scrubs the convective boundary layer inside the tube surface, yielding heat transfer coefficients three to five times those achievable in steady flow system. This permits modular construction of the pulse combustors, which can then be inserted into the sidewall of the gasifier vessel. Black liquor at 33 % concentration introduced into the bed undergoes a rapid sequence of vaporization and pyrolysis at a temperature below the melting point of inorganics (less than 650 °C). The bed is fluidized by steam and recycled gas. The black liquor droplets uniformly coat the surface of the bed solids, resulting in high rates of heating and pyrolysis. A porous char layer forms on the particle surface and is gasified by reaction with steam. Heat for the endothermic gasification reactions is supplied from pulse combustor resonance tubes, which are immersed in the fluid bed. Na_2SO_4 particles are reduced to Na_2S by reaction with CO and H_2. The Na_2S rapidly decomposes to H_2S and Na_2CO_3 .

Heating value of the gas rich in H_2 (63-67 %) is about 10 MJ/m^3. A high reduction efficiency can be achieved without the presence of a conventional molten char bed.

The gas produced is cooled and scrubbed to remove the hydrogen sulfide : the scrubbing solution is generated from the Na_2CO_3 solids discharged from the gasifier. The solution issuing from the scrubber is conventional kraft green liquor.

A portion of the product gas is recycled to the pulse combustor to supply heat to the gasifier. The balance of the product gas is combusted in a gas-fired boiler to generate steam and power. Preliminary heat and mass balances indicate an integrated plant net thermal efficiency greater than 67 %.

Besides a pilot plant in USA a pilot plant was in operation in the SAICA, Zaragoza mill in Spain. The MTCI technology is licensed in India to Esvin Advanced Technologies, Madras (79). A pilot plant was installed in Seshasayee mill in India. In SAICA soda straw black liquor was tested. In Seshasayee rice straw black liquor concentrated to 35 % concentration An alkali recovery efficiency of 99 % is reported (79). The duration of the short-term test was 24 hours. The results from this test are promising. In the SAICA mill the pilot plant was in operation for about one year (capacity 25 kg/h). Results of long term trials were not as expected owing to basically two problems (80) :

- high rate of tar formation, producing pollution in process condensates and fouling of the heat cooler, and
- agglomeration of bed solids after no more than 100-120 running hours.

The pilot plant was dismantled.

Apparently the technology is not yet ready for commercial operation. Once the above mentioned problems are solved the following advantages can be expected :

- modular construction of gasifier suitable to low capacities
- low concentration of feed black liquor thus avoiding silica scaling problems in evaporation
- recovery of alkali in powder form
- silica is converted to insoluble powder

- more electricity co-generation in combined cycle

The investment cost estimated in a UNEP case study are USD 1-1.5 million per one ton pulp/hour modules.

6.2.2 Wet cracking of black liquor

This method was developed by the Tianjin Institute of Light Industry, China (81). The system comprises a number of steps (Fig. 22). Black liquor at 16 % concentration is pumped by a high pressure pump (20 MPa) to a heat exchanger where it is heated by an already wet cracked liquor to 310 °C and further in a heating element heated by wet cracked gas heated to cracking temperature 360 °C. After discharging through a pressure reducing valve the following components are separated :

- Wet cracked gas 180-220 m^3/t organic solids (CO_2 30-35 %, CH_4 plus C_2H_6 39-49 %, H_2 20-24 %).
- Tar oil 80-120 g/t organic solids.
- Char powder and silica (solid particles) 80-120 kg/t organic solids .
- Yellow liquor, pH 7.5, containing mainly sodium bicarbonate and some sodium acetate and minor amount of sodium formiate. The yellow liquor is causticized to NaOH, but the recovery is low (about 50 %).

It is reported, that 80 to 95 % of organic matter and 96-99 % of silica is removed. The data of organic matter removal are optimistic in view of low soda recovery. The remaining sodium is obviously bound to aliphatic acids. The utilization of this as suggested is problematic and these compounds will be accumulated. It is proposed to incinerate the other organic products. It is claimed, that the investment cost may be about USD 500,000 for a mill of 5,000 tonnes/a capacity (price level 1986, in 1995 may be USD 1 million). For the same mill the power consumption of the high pressure pump is 50 kW, i.e. power consumption much less than in WAO.

The data are based on laboratory bench scale experiments. A pilot plant was planned, but no data are available.

6.2.3 The MKCR process

This process was developed and tested in pilot scale by Amrit Paper (India) (82). The black liquor from rice or wheat straw pulping is evaporated to about 40 % concentration or less. The black liquor after evaporation is mixed with rice husk in a

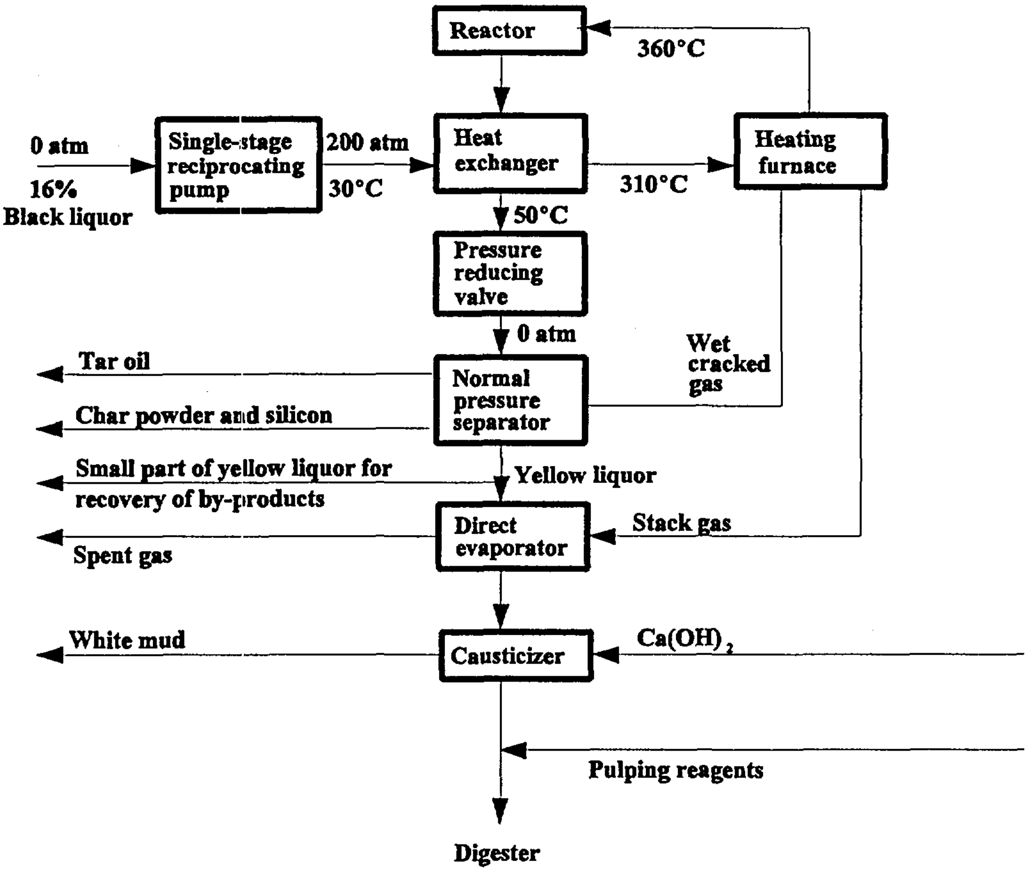


Fig. 22

WET CRACKING DEVELOPED BY TIANJIN INSTITUTE OF LIGHT INDUSTRY (CHINA) proportion 2:0.8 to 2:1.5 on w/w basis. Mixing with rice husk avoids high black liquor concentration. The husk used was air dried and had a heat value about 13.4 MJ/kg and contained about 15 % ash indicating a high silica content.

The semi solid mass obtained by mixing rice husk with black liquor was incinerated in a moving grate furnace at a temperature around 700 °C, but certainly less than 820 °C to avoid clinker formation. The ash is immediately removed from the furnace after combustion. The ash contains sodium carbonate and silica in proportion 60:40 to 75:25 . The ash is leached with water and clarified. The solution is heated to 80-90 °C and carbonated with carbon dioxide obtained by absorption of lime kiln flue gases into monoethanolamin (MEA).

The precipitated silica is filtered and washed with dilute acid (preferably with hydrochloric acid) to get high purity silica, which could be marketed.

The sodium carbonate solution is concentrated to higher concentration and causticized with lime. The recovery based on black liquor sodium content is about 80 - 85 %. It is claimed (82), that the investment cost for a 100 TPD pulp mill are about USD 900,000 (1993 level) pay back period 2.4 years, operational surplus about USD 350,000 per year. The system is not yet in continuous operation.

Advantages of the system is the low B.L. concentration required and incineration in a normal moving grate furnace. This, however, requires long-term operation to confirm smooth operation. It should be mentioned, that using of such high amount of rice husk significantly increases silica content of green liquor and consequently reduces chemical recovery efficiency due to loss of sodium in silica precipitate.

6.2.4 Chemical recovery by separation of organic and inorganic components of black liquor

All methods described in previous sections are based on incineration / complete oxidation of organic B.L. matter. Some authors investigated the possibility of separating a part of organic components and to recover inorganic chemicals. The separated lignin has some application possibilities such as drilling aid, briquette binder etc. However the market is limited and predominantly sulphonated lignin isolated from sulphite spent liquor or post-sulphonated alkali lignin is used. The alkaline black liquor after separation of lignin and hemicelluloses contain sodium carbonate, but a significant part of sodium is present as sodium salts of aliphatic acids, mainly as sodium acetate.

Venter and Klashorst (83) tested in laboratory scale some alternatives of organic matter separation and recovery of chemicals. One alternative is to precipitate hemicelluloses and silica by methanol, recovery of methanol, incineration of the filtrate and causticizing. Precipitation by methanol is a quite effective desilication. Another alternative is first precipitation of hemicelluloses with methanol, recovery of methanol, precipitation of lignin by carbonation with CO_2 and filtering of lignin. The filtrate can be evaporated, incinerated and finally causticized or sodium carbonate in the filtrate can be directly causticized. The first possibility - precipitation of hemicelluloses and lignin -

will result in low heating value of soluble solids. The second possibility - direct causticizing of filtrate - will recover only a part of sodium carbonate (may be 50-60 %) and as about 30 % sodium leaves with lignin and hemicelluloses and some sodium is bound in salts of aliphatic acids, which will accumulate in the alkali loop. This was not evaluated in the published work. As sodium recovery is low and the process has many steps the feasibility will depend on the possibility to market the lignin and hemicelluloses.

Basu (3) investigated separation of high molecular organic compounds by ultrafiltration and direct causticizing of the filtrate containing sodium carbonate and low molecular organic compounds. The sodium recovery will be low - probably around 60 %.

At present time in the SAICA straw pulp mill, Zaragoza, Spain precipitation of high molecular weight black liquor compounds by acification and polymer floculants is tested. The low molecular weight compounds are degraded and eliminated by biotreatment (most probably anaerobic). Lignin utilization as by-product is tested.

Recovery based on separation of high molecular organic compounds has little chance to be used in industrial scale. May be a few very small pulp mills could apply such methods, provided the lignin products can be marketed. This is discussed in UNIDO reports (4, 5).

6.2.5 Alternative and emerging pulping processes with simplified B.L. processing

Sodium based alkaline pulping is well established and reliable. However, chemical recovery requires high investment cost. Exchange of sodium against potassium base makes it possible to use black liquor as fertilizer. This in some cases, where agriculture can use this fertilizer, may be a solution for small mills (88). Ammonium bisulfite cooking is known and can be used for a wide variety of agricultural residues pulping (231). This technology was implemented in China (89). The spent liquor can used as fertilizer.

Organic solvents, such as ethanol or methanol can be used as pulping agent for wood and non-wood fibres (88, 90, 91, 92). The bulk of the lignin can be extracted with hot aqueous ethanol, but cooking to lower Kappa No. requires usually an acid catalyst. Several modification of this organosolv process have been investigated mainly on bench scale. Most advanced is probably the ALCELL process (90, 93, 94), which is tested in a 30 TPD demonstration plant in Canada. Preheated solvent that has been previously as pulp wash liquor is rapidly heated in the digester to 190 - 200 °C corresponding to 3.5 MPa pressure. The cooked fibrous material is washed with solvent in three stages and drained. The spent liquor is diluted with water to precipitate dissolved lignin. The separated filtrate enters a distillation tower. Alcohol, furfural and some acetic acid are recovered. The aqueous liquor contains carbohydrates, which as well as lignin show promise as chemical feedstock. The ALCELL process was tested for bagasse and wheat straw as well. The assumed economy of the process is based on marketing of by-products. However, the market for lignin preparations is limited (4, 5). The advantage of organosolv processes are by-products and low investment cost (no recovery boiler is required). Silica is retained mainly in the pulp and causes no problems. Disadvantage are cumbersome washing of pulp as washing with water would precipitate lignin. No steam is produced. No digester leaks and spills can be tolerated because of inherent fire and explosion hasard. At present time no industrial installation is known.

6.3 Conclusions and recommendations

From the discussed unconventional and emerging recovery processes only 3 processes are in industrial operation (for wood black liquor only) :

- DARS one industrial operation
- WAO two industrial operations
- CHEMREC direct gasification one operation

The second DARS operation - first for straw black liquor - failed. The reasons was most probably not failure of technology but inadequate equipment. All these unconventional processes are a result of long development and testing in a mill having high technical level.

An economically and technically acceptable way is to adjust these - or other emerging processes - for non-wood black liquors. The following actions may be considered :

- To evaluate the experience with the DARS process in the Burnie mill and to propose modification of the process to make it suitable for non-wood black liquors. To consider upgrading of the existing DARS pilot plant in CPPRI Saharanpur to continuous operation based on experience of the Burnie mill. The pilot plant should be, however, transferred to a mill in which it can be operated permanently for a longer period.

- To investigate first in laboratory scale possibility of reducing temperature, pressure and residence time in the WAO reactor by using oxygen-enriched air prepared by modern methods.

- To evaluate experience with black liquor gasification on industrial scale and if considered possible to investigate silica behavior in these process on laboratory scale.

- To evaluate material balances and inert compounds accumulation by computer simulation of wet cracking and lignin separation recovery processes using data of respective companies developing these processes.

7. COST - BENEFIT ANALYSIS OF CHEMICAL RECOVERY

The prices are as per IV. quarter 1995 and converted to USD :

1 USD = INR 33 (India)
1 USD = RMB yuan 8.25 (China)

7.1 Prices of chemicals, energy and manpower in China and India

Prices in India

Table 32

			Min.	Av.	Max.
Caustic soda	INR/ton		13,000	15,500	18,000
	USD/ton		394	424	545
Lime (CaO)	INR/ton		2,000	2,500	3,000
(Av. 70 %)	USD/ton		60.6	75.6	90.9
Sodium sulphate	INR/ton		1,200	1,300	1,500
	USD/ton		36.4	39.4	45.5
Limestone	INR/ton		1,000	1,100	1,200
(60 %)	USD/ton		30.3	33.3	36.4
Transport cost	INR/ton			750	
(lime)	USD/ton			22.7	
Fuel oil	INR/ton		5,000	6,000	7,000
	USD/ton		151.5	181.8	212.1
Live steam	INR/ton		450	500	550
(1.05 MPa)	USD/ton		13.63	15.15	16.67
Electricity	INR/MW		1,900	2,600	3,000
	USD/MW		57.6	78.8	90.9
Water	INR/1000 m^3			500	
	USD/1000 m^3			15.2	
Labour : Foreman	INR/day	180		USD/day	5.5
Operator	INR/day	125		USD/day	3.8
Unskilled	INR/day	80		USD/day	2.4

Note : All included (social security bonus etc).

Prices in China

Table 33

		Min.	Av.	Max.	
Caustic soda	RMB/ton	1,500	1,900	2,900	
	USD/ton	182	230	352	
Lime (CaO 75%)	RMB/ton	120	140	160	
	USD/ton	14.5	17.0	19.4	
Electricity	RMB/MW	250	325	400	
	USD/MW	30.3	39.4	48.5	
Live steam	RMB/ton	25	52	75	
	USD/ton	3.0	6.3	9.1	
					*in one case
Labour	RMB/man-month	550	620	750	1,100
(all inclusive)	USD/man-month	66.7	75.2	91	133

7.2 Investment cost for chemical recovery process

7.2.1 Pulp washing equipment

It is adviseable not to save money on washing equipment as agro-residues, especially wheat and rice straw are difficult to wash. In small pulp mills drum vacuum washers are used, manufactured by several companies (e.g. in India by Hindustan Dorr-Oliver). A list of small washing drums is shown in following table :

Table 34

WASHING DRUMS

Raw material	**Bagasse**		**Rice straw**		**Wheat straw**	
Capacity BD TPD	30	60	30	60	30	60
Washer size m	1.8x2.4	2.4x3.6	2.4x3		2.4x2.4	2.85x4.2
Washer surface m^2	14	28	23.3	44	18.6	37.6
Budgetary price INR million 1992 (ex works inc. conveyor, repulper)	1.5	1.95	1.68	2.6	1.55	2.52
Adjusted price INR million 1995	2.25	2.93	2.52	3.9	2.3	3.78

No prices of belt washers are available except for the new NACO inclined belt washer. The price for a 120 TPD NACO straw pulp washer in 1993 was USD 700,000. With 20 % inflation adjustment the estimated price in IV. quarter 1995 was USD 840,000 i.e. INR million 27.72 . The NACO washer has 3 washing stages and at a dilution factor DF 4 has a washing efficiency of 91-93 % and is comparable with a 4 stage (4 drum) washing line . The estimated cost of a drum washing line is about INR million 25 i.e. the investment cost is comparable with a belt washer.

Generally the cost of washing equipment will be about 9-10 % of the chemical recovery system (evaporation - incineration - causticizing).

7.2.2 Evaporators

Falling film evaporators are probably the better choice for non-wood black liquors. In Europe Wagner-Biro (Austria) claims, that FF plate evaporators are by 20 % cheaper, than LTV evaporators. FF plate evaporators are manufactured in India, but the undulated plates are imported and probably this is the reason that FF plate evaporators are by 100 % more expensive : (example for 80 TPD dry solids bagasse B.L.).

COST OF EVAPORATORS (India) Table 35

LTV 6 effects price approx.	USD	800,000	INR million	26.4
FF (plate) 7 effects price approx. (80 TPD bagasse B.L.)	USD	1,660,000	INR million	54.78

The price of FF evaporators from another company for various capacities

B.L. dry solids		70 TPD	160 TPD	300 TPD
Design, manufacture	INR million	76.8	120.0	240.0
Civil and electrical	INR million	9.0	15.0	21.5
Erection, commissioning	INR million	3.0	4.5	6.0
Total	INR million	88.8	139.5	267.5
Note : Number of effects		5	7	7

7.2.3. Conventional recovery boilers

An Indian company is supplying recovery boilers with superheater, generating 4.2 MPa steam, 420 °C. The approx. prices for various capacities are

Table 36

COST OF RECOVERY BOILERS (India)

B.L. Dry Solids capacity	70 TPD	160 TPD	300 TPD
Items	INR million		
Design, manufacture and supply of Boiler	65.0	95.0	150.0
Electr. precipitator	7.5	9.5	15.0
Civil	9.0	12.5	14.5
Electricals including motors, MCC and cabling inclusive of taxes and duties	6.0	8.0	10.0
Erection & commissioning	7.0	9.0	12.0
Chimney	2.5	3.5	4.5
Chemical dosing, salt cake handling system, etc.	1.5	1.5	1.5
TOTAL	98.5	139.0	207.5

Another Indian company is manufacturing recovery boilers with superheater generating 4.2 MPa steam and also without superheater and economizer generating 2.0 MPa steam.

The corresponding approx. prices for a boiler 80 TPD dry solids

Boiler 2.0 MPa	INR million	71.28
Boiler 4.2 MPa	INR million	86.13

7.2.4 Causticizing equipment

Several companies are manufacturing causticizing equipment - continuous and batch. Prices are in a wide range, depending on degree of sophistication. Batch causticizing line is cheaper, but suitable for small capacities only. Examples of prices are given below :

Table 37

COST OF CAUSTICIZING SYSTEM				
Pulp mill capacity TPD	30 - 40	40 - 60	60 - 80	60 - 65
Company	A	A	A	B
Causticizing line USD 1,000	200	250	335	414
Causticizing line INR million	6.600	8.250	11.050	13.662

Note: without civil works, electricals, pipe lines, erection, duties.
Estimate increase : 30 - 35 %

7.2.5 Cost of complete recovery system

The cost of a complete recovery system from Indian suppliers for a 4.2 MPa and LP steam system can be compiled from the above mentioned data (Tables 35-36-37) calculating 1.3 t B.L. dry solids per ton of pulp.

Table 38

COST OF RECOVERY SYSTEM INR million (USD million) with conventional recovery boiler			
	Altern. I	Altern. II	Altern. III
Capacity dry solid TPD	70	160	300
Capacity (approx.) TPD pulp	54	123	230
Recovery boiler 4.2 MPa (incl. ESP)	74	106	165.5
Recovery boiler LP steam	63	91	140
Recovery boiler erection (incl. civil, motors, duties etc.)	24.5	33	42
Evaporator train (FF)	76.8 (1)	120 (2)	240 (2)
Erection	12.0	19.5	27.5
Causticizing (3)	8.25	13.5	19.7
Erection	2.48	4.1	5.9
Equipment only (boiler LP) (without erection)	148.6 (4.5)	224.5 (6.8)	399 (12.1)
Equipment only (boiler 4.2 MPa) (without erection)	159 (4.8)	239.5 (7.3)	425 (12.9)
Recovery system total (boiler LP) (with erection)	187 (5.7)	296 (9.0)	474.4 (14.4)
Recovery system total (boiler 4.2 MPa) (with erection)	198 (6.0)	313 (9.5)	498 (15.1)

(1) 5 effect, steam economy 4.0 (2) 7 effect, steam economy 5.5 (3) erection cost 30 %

According information from European manufacturers the price of a recovery system can be calculated by the formula

$$\text{Price} = 14.5 \,.\, \left(\frac{A}{15{,}000}\right)^{0.6} \qquad A = \text{Capacity of mill}$$

Cost for a recovery system according this formula would be more than twice higher, than Indian prices. Estimates of Haskonig Consulting are by about 30-35 % higher (14), than Indian prices. Evidently, the low labour cost in India makes Indian prices for recovery equipment attractive. The price of the Epytek system for 100 TPD pulp when manufactured in India is estimated to about INR 160 million (84) (equipment only).

The investment cost for a fluid bed incineration system manufactured in India by Agro-Pulping-Machinery are presented in Table 39.

Table 39

COST (ESTIMATE) OF AGRO-ENDERS FLUID BED RECOVERY SYSTEM (USD 1,000)

Pulp mill capacity TPD	30-40	40-60	60-80
Evaporator	800	900	1,000
Fluid bed reactor	900	1,050	1,185
Causticizing	200	250	335
Engineering, erection, civil piping etc.	915	1,150	1,360
Total USD 1,000	2,815	3,350	3,880
Total INR million	92.895	110.550	128.040

The estimated price (according Agro-Pulping-Machinery letter) is significantly lower, than the price for a conventional boiler system. However, the system has no steam boiler and the operating cost will be higher.

The investment cost for other recovery systems have been estimated by Haskonig Consulting in 1994 (14). The following systems were evaluated

1. conventional recovery system
2. DARS (ferrite) process
3. CHEMREC gasification system
4. MTCI (Esvin) indirect gasification

The DARS system does not require causticizing and consequently no lime mud disposal. However Haskonig Consulting does not recommend a fluid bed reactor due to high fines generation (see section about DARS). The investment cost of the above mentioned systems are listed in Table 40. When compared with conventional recovery boiler the estimated investment cost of other systems are 60-65 % of the conventional systems. However, this estimate is not based on data of commercial installations. Japanese (76) authors estimate, that the cost for DARS system is 90-95 % of the conventional system. This estimate seems to be more realistic.

Table 40

ESTIMATED INVESTMENT COST - ALKALI RECOVERY SYSTEM
for pulp mill 30,000 BDMT / a

Plant cost MUSD / system No (page 114)	1	2	3	4
Evaporation	1,500	1,500	1,500	1,500
Soda recovery boiler or ferrite reactor with waste heat boiler	7,000	4,500	3,500	3,000
Causticizing / hydrolysis	1,500	750	1,500	1,500
Total	10,000	6,750	6,500	6,000

The investment cost for WAO (wet air oxidation) are considerably higher when compared with a conventional system.

7.3 Production costs of recovered chemicals
(incineration in recovery boilers)

The chemical recovery system is a sub-system of pulp production, therefore simplified production costs calculation is applied. Factory overheads (indirect fixed costs) and administrative overheads are not included, as these are calculated in pulp production. Royalties, research and development costs are included in equipment costs. Cost calculations are based on prices of Indian equipment, chemicals and energy (Table 32). All calculations are related to dry solids and not to pulp to exclude variations of pulp washing efficiency.

7.3.1 Manufacturing (working) conditions

Agro-based pulp mills are using a variety of raw materials. Consequently, chemical charge, yield, washing efficiency etc. differ considerably. To make possible comparison of chemical recovery systems all calculations are based on B.L. dry solids and following cooking conditions :

Chemical charge on raw material NaOH %	16 % i.e. 12.4 Na_2O
Inorganic ballast compounds (Na_2CO_3) 10 % on Na_2O	2.12 % Na_2CO_3
Total inorganic charge on raw material	18.12 % (NaOH + Na_2CO_3)
Total Na_2O charge	13.6 %
Pulp yield	50 %
Dissolved organic substances t/t O.D. pulp	1,000 kg
Dissolved Na_2O kg/t O.D. pulp	272 kg
Dissolved inorganics kg/t O.D. pulp	362 kg
Total dissolved solids TDS t/t O.D. pulp	1,362 kg

Chemical losses in recovery system :	Bagasse	Straw
Recovery boiler	0.5 %	0.5 %
Recausticizing (without desilication)	2.5 %	3.0 %
Others	1 %	1.5 %
Total	4 %	5 %

Consumption data :	
Electricity kWh/t dry solids	140 kWh
(Note : Data of companies are in the range 110 - 170 kWh/t TDS)	
Steam in causticizing kg/t dry solids	240 kg

7.3.2 Evaporation and incineration

Table 41

ALTERNATIVES OF EVAPORATION AND INCINERATION

Alternative	Black liquor concentration %			No. of effects	Steam economy t_{water} / t_{steam}	Steam surplus t / t TDS
	Weak	Evaporated	Concentrated Direct. Evap.			
B1 (bagasse)	10	45	60	5	4	+ 1.16
S1 (straw)	8	45	52	5	3.2	- 0.16
B2 (bagasse)	10	45	60	7	6	+ 1.81
S2 (straw)	8	45	60	7	5.4	+ 1.16
E (bagasse)	10	60	-	6	5	+ 1.87

- deficit

Evaporation of alternatives B1, B2 follows basically an Indian company proposal with falling film evaporators. Alternative S1 (wheat straw) is basically alternative B1, S2 is as B2, with frequent cleaning of evaporator bodies. Alternative E (bagasse) is based on a paper presented by I. Huercanos (Epytek) on the PAPEREX '95 Conference, New Delhi (Dec. 1995) with a special falling film concentrator evaporating indirectly bagasse B.L. to 60 % concentration. Application for wood B.L. only till this time. Incineration alternatives are related to Table 21A, 21B. All alternatives are without desilication and without electricity co-generation. Fuel oil consumption for alternatives B1, B2 are 7 kg/t dry solids and 20 kg/t dry solids for alternative S1. No fuel oil for alternative E.

7.3.3 Recausticizing

Input of Na_2O with 1 tonne dry solids (losses in recovery boiler deducted)		198 kg
Theoretical CaO consumption kg/t dry solids		180 kg
Availability 70 %		
Lime consumption kg/t dry solids		257 kg
Total Na_2O kg/t dry solids in white liquor	bagasse	191 kg
to digester (losses deducted)	straw	189 kg
Active NaOH kg/t dry solids in white liquor	bagasse	226 kg
	straw	223 kg

7.3.4 Operating (direct) costs per tonne of dry solids (based on Indian prices page 106)

		Alternative				
		B1	S1	B2	S2	E
Lime (70 % availability)	INR	835	835	835	835	835
Electricity	INR	286	364	286	364	286
Fuel oil	INR	42	120	42	120	-
Steam (incl. caustic.) saving - / consumption +	INR	- 460	+ 200	- 785	- 460	- 815
Net operating cost INR/t dry solids		703	1,519	378	859	305

7.3.5 Investment, capital and personnel costs

The investment cost are based on Table 39. A low pressure (LP) recovery boiler is considered without electricity co-generation. Alternatives I - III are for different bagasse B.L. dry solids capacity. Dry solids capacity per year is based on 330 working days.

Alternative	I	II	III	E
Dry solids tonnes per day	70	160	300	110
Dry solids tonnes per year	23,100	52,800	99,000	36,300
Investment costs INR million	187	296	474	165 *
Depreciation 12 % incl. spares INR million	22.440	35.520	56.880	19.8
Interest on investment cost 17 % INR million	31.790	50.320	80.580	28.1
Total capital costs INR million	54.230	85.840	137.460	47.9
Personnel costs per day INR	7,200	7,200	7,200	7,200
Personnel costs per t/dry solids INR	103	45	24	65
Capital costs per t/dry solids INR	2,348	1,626	1,388	1,317

* Investment corrected against PAPEREX `95 data (increased cost of erection).(84)

This calculation clearly indicates economy of scale. The combined capital and personnel costs per tonne dry solids at a capacity 99,000 tonnes dry solids/a are just 58 % of the costs per tonne dry solids at capacity 23,100 tonnes dry solids/a.

Table 42

TOTAL PROCESSING COSTS OF DRY SOLIDS AND PRODUCTION COSTS OF CAUSTIC SODA

Approx. pulp capacity t/day	50 - 55		120 - 130		230 - 240	90
Dry solids t/day	70		160		300	110
Alternative	B1	S1	B2	S2	B2	E
Capital costs INR/t TDS	2,348	2,348	1,626	1,626	1,388	1,317
Personnel costs INR/t TDS	103	103	45	45	24	65
Net operating costs INR/t TDS	703	1,519	378	859	378	305
Total processing costs INR/t TDS	3,154	3,970	2,049	2,530	1,790	1,687
Direct operating costs INR/t caustic soda	3,110	6,811	1,673	3,852	1,673	1,349
Total production cost caustic soda 1 tonne INR	13,956	17,802	9,066	4,345	7,920	7,465
Production caustic soda t/a	5,220	5,151	11,932	11,714	22,374	7,601
Savings INR million / a	11.975	- 7.994	92.17	57.450	186.370	66.774
Pay-back period ; years	15.6	Loss	3.2	5.2	2.54	2.47

- loss

Purchased caustic soda price INR 15.550 + 700 transport cost.

Note : Alternatives B1, S1, B2, S2 are based on prices of Indian suppliers.

Alternative E is based on approx. price of Epytek System published on PAPEREX '95 Conference (New Delhi, Dec. 1995) by J. Huercanos presuming licence manufacture in India (no licence agreement signed till this time).

Conclusions

The feasibility of chemical recovery (using recovery boiler) at various dry solids capacities and different evaporation conditions is presented in Table 43 for bagasse and wheat straw. All alternatives are based on evaporation in film (FF) evaporators. Alternative B1 is bagasse weak B.L. 10 % evaporated on FF evaporator 5 effect line to 45 %, steam economy 4.0 water per 1 tonne of steam. Alternative S1 is basically as B1, but wheat straw B.L. (weak B.L. 8%) with steam economy 3.2 due to frequent cleaning of evaporator. Alternatives B2 and S2 are based on evaporation 7 effect body (straw B.L. steam economy 5.4 , bagasse B.L. steam economy 6.0). Alternative E is based on lower investment cost.

Table 43 clearly shows the influence of economy of scale. At 70 t/day dry solids bagasse B.L. recovery has a pay-back period 15.6 years, but at 160 t/day TDS the pay-back period is 3.2 years only. Capital costs are much higher, than operating / processing costs.

The difference between wheat straw B.L. and bagasse B.L. is significant, as straw B.L. has lower weak B.L. concentration and generally is evaporated to 52-53 % only due to high viscosity. Consequently, the system has steam deficit and would operate with loss. At 70 t/day TDS recovery of wheat B.L. is operated with loss, but at 160 t/day TDS the pay-back period is acceptable, but higher than for bagasse.

Alternative E with evaporation of bagasse B.L. to 60 % concentration is resulting in higher steam surplus and, consequently in lower direct (operating) costs. Pay-back period is low also as a result of slightly lower investment cost.

The pay-back period at low capacity is on same level as presented by A. Panduraga (TMT India) on Recovery Seminar 1995 (15). In the TMT system the direct costs are higher (steam deficit), but investment and consequently capital costs lower. Pay-back period about 12.5 - 14.0 years for bagasse B.L. recovery.

Production costs and pay-back period may be reduced by soft-loans. At 8 % interest in alternative B1 the caustic soda production cost is reduced to INR 10,730 /t and the pay-back period from 15.6 to 6.5 years.

Desilication may improve evaporation economy of wheat straw black liquor, but is feasible at higher capacities only (see page 89, 90).

These calculations indicate, which sub-processes should be improved to increase feasibility of small scale agro-based chemical recovery

- improvement of washing to increase black liquor concentration at least to 10 % and increase recovered dry solids in B.L.
- reduction of B.L. viscosity to enable evaporation to higher concentration and better steam economy, preferably by modification of cooking (heat treatment is expensive)
- evaporation to higher concentration (say 60-62 %) in a concentrator less sensitive to scaling
- steam deficit should be avoided, as this increases operating cost resulting in loss.

7.4 Production costs of recovered chemicals in fluid bed recovery (based on Indian prices)

The investment costs for a fluid bed recovery system are listed in Table 38 (page 113). The same cooking conditions are considered as on page 111.

The chemical recovery conditions are as follows :

Weak black liquor concentration		10 %
Evaporated black liquor concentration		25 %
Evaporated water t/t dry solids		6
Steam economy of evaporation	t_{water} / t_{steam}	3.2
Steam requirement t/t dry solids		1.875
Electrical energy requirement	kWh/t TDS	180
Chemical losses		
- incineration		3 %
- causticizing		2 %
Total		5 %
Alkali as Na_2O to causticizing	kg/t TDS	185
Lime requirement 70 % availab.	kg/t TDS	255
Steam in causticizing	kg/t TDS	240

Operating (direct) costs per tonne of dry solids

Lime (70 %)	INR 3250 per tonne	829
Electricity	INR 2.6 / kWh	468
Steam		1,057
Others (charcoal etc.)		50
Total		1,937

Capital costs

Dry solids / day / year		43 / 14,200	63 / 20,790	88 / 29,040
Depreciation 12 %	INR mil/a	11.147	13.266	15.364
Interest rate 17 %	INR mil/a	15.792	18.793	21.769
Capital costs total	INR mil/a	26.939	32.059	37.131
Capital costs INR per 1 tonne TDS		1,897	1,542	1,278
Personnel per day	INR	5,600	5,600	5,600
Personnel costs per 1 tonne TDS INR		130	88	63

Table 43

TOTAL PRODUCTION / PROCESSING COSTS OF DRY SOLIDS AND CAUSTIC SODA			
Capacity pulp TPD	30 - 40	40 - 60	60 - 80
Dry solids TPD	43	63	88
Capital costs INR/t TDS	1,897	1,542	1,278
Personnel costs INR/t TDS	130	88	63
Operating (direct) costs INR/t TDS	2,404	2,404	2,404
Total processing cost INR/t TDS	4,431	4,037	3,745
Total production costs INR for 1 tonne caustic soda	18,159	16,545	15,348
Production of caustic soda t/a	3,462	5,072	7,085
Savings INR million/a	- 6.426	- 1.496	6.390
Pay-back period, years	-	-	20

- loss

These calculations are based on Indian equipment prices without waste heat boiler. Operating (direct) costs are higher with fluid bed reactor as no steam is generated. Investment cost are lower, but production cost are higher than with conventional (recovery boiler) technology due to high direct costs. Economy of scale is significant. Savings are at a capacity 88 t dry solids / day but pay-back period is too high. Situation may improve at higher capacities. Also a waste heat boiler will reduce direct costs. No data for such a alternative are available.

The fluid bed system is at present time in operation for bagasse black liquor only.

7.5 Feasibility of biological treatment of black liquor

Chemical recovery trough incineration of black liquor is the best water pollution abatement process as it eliminates about 90 % of organic substances generated in pulping i.e. about 90 % of both BOD and COD. The efficiency of eliminating BOD and COD is dependent mainly on washing efficiency.

Biological treatment - activated sludge (aerobic) or anaerobic treatment - eliminates 85-90 % BOD but only 60-65 % COD. A substantial part of resistant organic substances and all inorganic substances are not eliminated.

Chemical recovery is resulting in savings. Only in case of very low weak black liquor concentration and low firing concentration the system operates with loss as the steam generated by incineration of black liquor does not cover the steam consumption in evaporation of black liquor as it is in some cases especially in straw pulping (see alternative S2, Table 42). If the pulp mill capacity is very small (about 50 TPD) than such a system is working with a loss (see alternative S2, Table 42). The expenditure for processing black liquor from one tonne of pulp is about INR 450 per tonne of pulp.

Treatment of pulp mill effluent by aerobic activated sludge in Indian conditions was discussed in the IPPTA Convention Issue 1987. According Palakshappa and Chandrashekar (see page 94) the processing costs of 1 kg BOD reduction in 1987 were INR 1.06 / kg BOD and the investment costs for a BOD loading capacity 16.680 kg per day were INR million 25.

The BOD generation in bagasse pulping is about 310 kg BOD per tonne of pulp, i.e. in alternative S2 the BOD loading would be 16,120 kg per day. The BOD reduction at 90 % efficiency would be 280 kg per tonne of pulp. At 1987 price level the processing costs were in such case 297 kg per tonne of pulp. About 70 % of these cost was electricity. In 1995 the power prices increased from INR 1.00 / kWh to INR 2.6 / kWh. Consequently the BOD reduction cost may be doubled to about INR 600 / t of pulp. Total cost for reduction 1 kg BOD will include capital resulting in total cost for black liquor processing per one tonne of pulp around INR 800. The cost for activated (aerobic) sludge treatment are considerably higher, than the cost of black liquor processing in chemical recovery in the most unfavorable conditions (alternative S2, Table 42). However the investment cost for a capacity 52 TPD for activated sludge system may be just about INR million 30 - 35 which is only a fraction of investment cost for a chemical recovery. It can be concluded, that aerobic biological treatment is not an acceptable alternative to chemical recovery based on incineration of black liquor.

Anaerobic digestion of pulp mill black liquor is in operation in two mills. In the Spanish SAICA mill (86) (soda straw semichemical pulp) and Indian Pudumjee 40 TPD bleached bagasse soda pulp mill. In the anaerobic digestion diluted black liquor is processed at elevated temperature (31.5-39 °C). Retention time in the digester is 4-5 days. BOD reduction is 85-90 %, COD reduction is about 60-65 %. A part of organic substances is converted to methane. In Pudumjee mill 10,000 m^3/day biogas is generated containing up to 70 % methane which is used in steam boilers with fuel oil. Anaerobic digestion requires considerably less electrical energy and less nutrients than aerobic treatment. Only 10-20 % sludge is generated when compared with aerobic treatment. In Pudumjee mill 10,000 m^3 biogas is generated (heat value 5,600 kcal/Nm^3). The heat generated is about 4.2-4.5 GJ/t of pulp. The best alternative in chemical recovery (Table 41 and 42) has a heat surplus about 5.0 GJ/t of pulp, the next alternative about 4.5 GJ/t of pulp (after deduction of steam for evaporation of black liquor and for causticizing). Heat surplus in chemical recovery is slightly higher. For comparison the heat surplus in a modern wood pulp mill is about 11 GJ/t of pulp. The investment cost in Pudumjee in 1988 was INR million 25.0. The pay-back period is 6 years. It can be concluded, that anaerobic treatment can be an alternative for very small mills (about 50 TPD pulp). However pollution abatement is not on a high level, as nearly all lignin and all inorganic compounds are discharged to the recipient. For mills of 100 TPD or higher capacity anaerobic treatment is not a viable alternative. SAICA mill is also interested in a more efficient pollution abatement.

ANNEX - I

LITERATURE

LITERATURE

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ANNEX - II

MAIN CHEMICAL RECOVERY EQUIPMENT SUPPLIERS IN P. R. CHINA AND INDIA

(Note : Suppliers in Europe and America are listed in all Pulp and Paper Industry directories)

MAIN CHEMICAL RECOVERY EQUIPMENT SUPPLIERS IN P. R. CHINA

A. Tianjin Light Industry Machine Work's
272 Xiqing Dao
Xijiao District
Tianjin, 300380 China
Tel.: +86 22 791042
FAX: +86 22 792930

Manufacturing programme:

a) Globe (spherical) digesters for cooking agro-residues
   Stationary digesters for reed and simular materials
   Blow tanks and other auxiliary equipment for cooking room
   Continuous SUNDS-Defibrator type horizontal tube digesters
b) LTV evaporators (IV-V effects lines)(240-660 m^2)
   Short tube evaporators (IV effects lines)(310-390 m^2)
   Disc contact evaporators 80-120-185 m^2
c) Causticizing equipment continuous and batch
d) Electrostatic precipitators for recovery boilers
e) Plate type falling film evaporators (new own development)

Delivery list of FF:

Tai-Zhon Paper Mill
Chongzing Paper Mill
Quing-Zhon Paper Mill
Tai-Juran Paper Mill
Liu Jiand Paper Mill
Nanning Paper Mill
Xui-Zhon Paper Mill
Shang-Feng Paper Mill

Large evaporator line (FF) for Indonesian mill.

B. Wuhan Boiler Works
290 Wuluo Road
Wuhan, 430070 China
Tel.: +86 27 713822
FAX: +86 27 716 938

Delivered most of chemical recovery boilers in China.
Twin-drum waterwall boilers with vortex spray, 37.5 - 450 TDS/day.

C. Zhi Gun Light Industry Machine Work's
30 Da An Street
Zhi Gun, Sichuan Province, 643010 China
Tel.: 221401

Rising film evaporators

4 effect	180 m^3/each
5 effect	300 m^3/each
5 effect	400-550-700 m^2

Falling film evaporator 550 m^2/effect
Recovery boilers delivery list:
- Five small recovery boilers ZHP 11, 12, 16.
in Guanxi, Hunan and Fujian Provinces:
- Guiping Sugar Refinery Paper Mill, Guanxi Province
- Hongjiang Paper, Hunan Province
- Guangze Paper Mill, Fujian Province
- Jianyang Paper, Fujian Province
- Xiangyin Rengmin Paper Mill, Hunan Province

30 Da An Street
Zhi Gun, Sichuan Province, 643010 China
Tel.: 221401

Rising film evaporators

4 effect	180 m^3/each
5 effect	300 m^3/each
5 effect	400-550-700 m^2

Falling film evaporator 550 m^2/effect
Recovery boilers delivery list:
- Five small recovery boilers ZHP 12
in Guanxi, Hunan and Fujian Provinces:
- Guiping Sugar Refinery Paper Mill, Guanxi Province
- Hongjiang Paper, Hunan Province
- Guangze Paper Mill, Fujian Province
- Jianyang Paper, Fujian Province
- Xiangyin Rengmin Paper Mill, Hunan Province

D. An Qui Machinery Work's, Shangdong
Drum vacuum washer

Filter area m^2		10	15	20	25	30	35
Capacity t/d	wheat straw	20-30	30-45	40-60	50-75	60-90	70-105
	wood pulp	40-50	60-75	80-100	100-125	125-150	140-175
Motors (all) kW		13.7	13.7	18.7	18.7	22.7	22.7

Inlet consistency	1 - 1.5 %
Outlet conc.	10 - 12 %

E. Ji Ning Light Industry Machinery Works
Shangdong Province
Belt vacuum washer

F. Hang Zhou No 1 Light Industrial Machinery Works
ZNDA horizontal belt washers

BELT VACUUM WASHER BASIC DATA			
	ZND1A	ZND2A	ZND3A
Area m^2	12	18	24
Inlet cons. %	3 - 4		
Outlet cons. %	15 - 19		
Capacity t/d			
rice straw	12	18	24
wheat straw	20	30	40
reed	60	90	120
wood	84	126	168
Dilution factor t water/t pulp	2 - 3		
Belt speed m/min.	2.6 - 26	3.9 - 39	5 - 50
Length x width m	11.5 x 2.8	16.5 x 3.1	21 x 3.3

MAIN CHEMICAL RECOVERY EQUIPMENT SUPPLIERS IN INDIA

ENMAS PROCESS TECHNOLOGIES LTD.
V. Floor Guna Buildings Annexe
304-305 Anna Salai
Teynampet, Madras - 600018
FAX: +91-44-4342448
Ahlstom type recovery boilers (for bagasse 1 supplied, 2 on stream) LTV and FF evaporators supplied to several mills, but only LTV for agro- based mills
Desilication system (type CPPRI-UNIDO) - acquired know-how

TMT (India) Ltd.
5-8-113, II Floor 21 Century Compex, Nampally
Hyderabad - 500001 A.P. FAX: +91-40-203100
LTV and FF (plate) evaporators. Recovery boiler, causticizing. one system in operation

CHEMCON (P) LTD. a subsidiary of
CHEMPROJECTS DESIGN AND ENGINEERING (P) LTD.
Gopal Deep, 17 Panchshilla Shoping Centre
New Delhi - 110017 FAX: +91-11-6435289
EPYTEK (Spain) type FF evaporators)
Air-cooled refractory recovery boiler (bagasse application)

PAS Construction and Engineering (PVT) LTD.
803 Madhuban, 55 Nehru Place
New Delhi - 110019 FAX: +91-11-6463981
LTV evaporators. FF evaporators Axel Rosenbad type
Several application, but not for agro-based B.L.

HINDUSTAN DORR-OLIVER
Dorr Oliver House, Chakala, Andheri (East)
Bombay - 400099 FAX: +91-22-8365659
Vacuum drum pulp washers
Causticizing equipment
Planned: BELLMER type double wire washer

AGRO PULPING MACHINERY (P) LTD.
23 Anu Apartement, 4th Floor
39-B, Chevalier Sivagi Ganesan Road
T. Nagar, Madras - 600017 FAX: +91-44-4345578
Evaporators, Fluid bed reactors,
Causticizing equipment
Two systems to be supplied in 1996 for bagasse and bagasse - wheat straw mixture.

CHELLAM MARKETING AND CONSULTANCY PVT.LTD.
Krishna Complex, 4th Floor
39 - B, South Bong Road, madras - 600017 FAX: +91-44-4345578
DELKOR type horizontal belt washer (used in South Africa for bagasse pulp)

BHEL - Bharat Heavy Electricals Ltd.
General Manager / Engineering and Commercial
Tiruchirappali 620014 T.N. FAX: +91-431-552642
Recovery boilers (L.E. type) 100-2500 tons per day D.S.
Several applications for medium and large mills

ABB-ABL LTD. (Babcock)
P.O. Durgapur - 713 206
Dist. Burdwan, West Bangal
Fax: + 91-343-6286, 5834
Supplied recovery boiler 100 TDS/day
for Mandya bagasse pulp mill

SWEATHA ENGINEERING LTD.
Plot No.1961-B, Asiad Colony, Vijaya Complex, 2nd Floor, Anna Nagar West,
Madras 600 101 FAX: +91-44-6268377
Design & supply of Evaporators.
Supplied one MEE unit to Shree Vindhya Papers

ALFA LAVAL INDUSTRY
Bombay-Pune Road, Dapodi,
Pune -411 012 FAX: +91-212-779479
Supplier of Evaporators.
Supplied MEE units to Hindustan Newsprint LTD (HNL) & TNPL.

TRIDENT ENGINEERING (PVT) LTD.
No.37, 53rd Str., Ashok Nagar,
Madras -600 083 FAX: +91-44-4896140/4821897
Design & Supply of Chemical Recovery Boilers

ANNEX - III

DESCRIPTION OF CHEMICAL RECOVERIES USING NON WOOD FIBROUS RAW MATERIALS

SMALL PULP MILLS IN CHINA

Visit of Xin-Hua Paper Mill, Shanghai

The mill is producing 55-60 t/day unbleached and 44-45 t/day bleached pulp from a mixture of 70% wheat straw and 30% of rice straw.

The SiO_2 content in raw material is about 10% and 30-40% in the dust which represents about 10% of the raw material. 6% of the dust are collected by dry cleaning - by blowing air from the bottom of the transport chain conveyor.

The mill has 5 digesters each of 40m^3 volume. The chemical charge is 14% NaOH and 2-3% Na_2SO_3. The raw material to liquor ratio is 1:3, cooking time 2.5 h at 150°C. The yield of unbleached pulp is 50% of bleached pulp 37%. Silica in black liquor dry solids is 4%, but with addition of 2-3% Na_2SO_3 is about 3% only. Inorganics in dry solids are about 35-40%. The heat value HHV is about 3,000 kcal/kg.

By addition of Na_2SO_3 the viscosity of black liquor is reduced and also less silica is dissolved in the black liquor. The cooking is actually a low-sulphidity kraft pulping as sodium sulphite and the derivatives of this compound are reduced in the recovery furnace to sodium sulphide. The incineration process has to be reductive as otherwise sodium sulphite would be oxidized to sodium sulphate and accumulated. The conc. of B.L. from digester is 16-18%.

The unbleached pulp is washed on two horizontal belt washer manufactured by Xi An Paper Machinery Factory (Shan Xi province). Belt washer data:

speed 30-35 m/min	width 1.35 m	length 18 m	surface 24 m^2
Capacity: 30-35 t/day	Synthetic wire mesh 28 (per cm)		

The belt washer has 5 sections each has 2-3 showers; countercurrent washing. The filtrate from the 1° and 2° is going to evaporator and blow tank. The dilution coefficient is 3.0-3.5 m^3/t of pulp. The inlet consistency is 3%, outlet 12%. The loading capacity is up to 1.6 t/m^2. Higher concentration result in a non-uniform mat, at lower concentration the pulp overflows. The fibre content in filtrate (B.L.) is held preferably at 50 mg/l. In contrary to previous publications the belt washer has a low washing efficiency (80-85%, most probably just 80%). The shower liquid is not covering the mat uniformerly. The construction gives an impression being a temporarily one. The conc. of weak black liquor is about 8% (cross calculated as mill data are not reliable). The mill measures °Be reportedly at 60°C, which gives data out of range.

The weak black liquor (W.B.L.) is evaporated on a 4 effect short tube vertical evaporator with natural circulation. The evaporator line has a surface condenser (pressure in IV effect 0.05 MPa). The evaporator was manufactured by GUANG DONG Light Industry Factory (Canton). The first two bodies have an evaporation surface 600 m^2/each, the III-IV 500 m^2/each. Steam is flowing I-II-III-IV. Black liquor flow is a mixed flow (two flows).

One flow is W.B.L. to III and IV effect and to semi-strong B.L. tank. From this tank to I and II effect. In the parallel flow the W.B.L. is fed to I and partly to III effect to keep proper level and circulation in IV effect. The parallel flow of W.B.L. is cleaning evaporator tubes in I and II effect after using these effects to evaporate semi-strong B.L. to strong B.L. By this alternate evaporation reportedly an evaporation rate 8-14 kg/m^2/h is reached. The S.B.L. has a conc. 43-45%. The steam economy is 2.2-2.5t of water/ton of steam (lower than reported in previous publications). The volume of W.B.L. is 30 m^3/h, evaporated water about 24-25 m^3/h. Residual alkali is 12-16 g/l NaOH.

The B.L. heat value is about 3,000 kcal/kg. The silica content 4% on D.S. With addition of Na_2SO_3 it can be reduced to 3%. Inorganics in D.S. are 35-40%.

The evaporators tubes are cleaned with high pressure water (40-70 MPa).The B.L. from the evaporator line is further evaporated from 43-45% to 51-52% on a cascade evaporator (flue gas inlet 230°C outlet 150°C).

The recovery boiler is a waterwall (membrane type) boiler with two drums. The sectional size of the furnace is 2,240x2,240 mm. The boiler has three vortex type spray nozzles (suspension combustion) mounted on the front and side walls at a height 7000mm above furnace floor. The boiler has primary, secondary and tertiary air (1° and 2° preheated from 130°C to 250°C). The B.L. conc. is just 50-52% at 105°C to keep viscosity in acceptable limits. Char bed is 600-700 mm high. As V.T.E (volumetric thermal expansivity) is low when compared with wood. Primary and secondary air should be above 200°C. The spray nozzle should not be too small as the fly ash has low fusion point and may plug boiler tubes. The boiler has an electroprecipitator with a 95% efficiency. The flue gases 15,000 m^3/h contain 150 mg/m^3 particles. Soot-blowing is by air.

The green liquor is causticized in a continuous process. The CaO consumption is 1.6-1.7 kg/kg NaOH. The lime mud is filtered and washer on a belt filter (Jiang Dong Machinery, Shanghai) to 43% dryness. The NaOH loss is 3-5%. Causticity 85-87% causticizing efficiency about 75%. White liquor composition: 75 g/l NaOH, 8-10 g/l Na_2S, 15-20 g/l soda.

The overall chemical recovery efficiency is estimated by the mill to 50-55%. When compared with above mentioned figures if seems to be too low and by the author of this report is estimated to 70%.

The price of NaOH is 1,500 - 1,600 RMP/t, CaO 140 RMB/t, steam 80 RMB/t (0.8 MPa), electricity 0.51 RMB (including tax) labor cost 1,500 RMB/month.

Pulp mill of the MIFENG GROUP CORPORATION

The Mifeng Group is a large corporation producing various speciality papers from own and market pulp. It is also active in another industrial sectors such as cement.

The pulp mill is producing 8,000 BDMT/a i.e. about 25 TPD from wheat straw, reed and Chinese alpine rush. The straw is dedusted in a dry process blowing air through the mat of straw on the chain conveyor. Wheat straw is cooked separately in 4 rotary globe digesters 40 m^3 each using 13.5% NaOH (without Na_2SO_3). Reed is cooked in 2 stationary digesters (50 m^3 each) using direct steam. The cooking temperature is 170°C 5 has in stationary digester and 3 hrs in globe digester. The liquor to raw material ration in straw cooking is 3:1 and in reed cooking 5:1.

Washing is 4° stage on two lines and the black liquor is combined. The washers are of drum type. The operation is not appropriate, the showers does not cover the mat uniformely. The water is not sucked properly, it is partly flowing down on the surface diluting the B.L. in the van of the washer-filter.

The water temperature is low (about 60°C). It is estimated, that the washing efficiency is just 80%.

The concentration of straw W.B.L. is about 7° Be' (about 8%) and of reed W.B.L. about 6-7° Be' (maybe below 8.0%).

Besides chemical pulp from wheat straw and reed the mill is producing semichemical pulp from rice straw, but the black liquor is not incinerated, just treated biologically.

The evaporator line is 4 body 4 effect, LTV raising film, with vacuum pump 0.098 MPa each body has 153 tubes, 180 m^3 heat transfer surface. The steam flow is I-II-III-IV. Black liquor flow is combined in cycles (similar as in Xin Hua Mill). In one cycle semi-strong B.L. is evaporated on bodies I-II to 220 Be' at 90°C (i.e. about 26° Be' at 150°C and 34-36 % conc.). In the other cycle weak black liquor is evaporated on bodies I-II dissolving or suppressing scaling. Semi-strong B.L. is prepared in bodies III-IV.

The strong black liquor from the evaporator is further concentrated on a cascade evaporator to about 46-48% conc. (25-27° Be' at 95°C). The concentrated B.L. is incinerated in a recovery boiler/smelter of total height 16m. The bottom part is an air-cooled jacketed, round, refractory smelter, inside diameter 2 m. The cooling air heated in the jacket to 200°C is used as primary air. The refractory smelter is removable and is combined with a water-walled boiler with electrostatic precipitator.

The primary objective of the design is to maintain the hearth temperature as high as possible at and above the char bed to sustain continuous combustion. Typical operation conditions are as follows:

B.L. to cascade	concentration	35%
B.L. to be fired	concentration	46/48%
	temperature	90-100°C
Nozzle	type	vortex
	diameter	10 mm
	pressure	180-240 kPa
Air temperature	primary	250-300°C
	secondary	180-240°C
Gas temperature	at boiler bank inlet	500-600°C
	at ECO exit	260-300°C
	at EP inlet	140-150°C
Smelt	temperature	850-870°C
EP	efficiency	98%
Area heat load		3,940 MJ/m^2h

The furnace was retrofitted in 1983 and is in operation since then. Continuous combustion has been achieved. No auxiliary fuel is needed.

The steam pressure is 0.7 MPa, heat value of B.L. solids 12.57 MJ/kg. Several recovery boilers of this type have been installed in China (see chapter: Equipment manufacturers in China).

SMALL PULP MILLS IN INDIA

Vindya Mill

The recovery system supplied by Enmas was installed in the existing pulp mill in 1994 and is in full operation since November 1994.

The pulp mill is producing 60 TPD bagasse pulp. The bagasse storage is dry and the depithing is also dry in PEADCO type vertical depithers with 10mm perforations. The pulp mill has five 60m^3 globe digesters. The alkali charge is 15-16% NaOH plus 0.05 anthraquinone. In the future the mill is planning cooking without anthraquinone at 16% sulphidity. The liquor to bagasse ratio is 2.5 to 3:1 adjusted by water.

The cooking temperature is 165-168°C, the permanganate K number about 11 (Kappa No. 14-15). The RAA is about 6 g/l. Bleaching is with Ca-hypochlorite and chlorine CHH (adding NaOH for maintaining pH). Total active chlorine 8-9%, elementary chlorine 4-5%.

Washing of unbleached pulp is on Dorr Oliver drum washers 8'dia, 10'face, 3 stage. Chemical loss in washed pulp about 15 kg Na_2SO_4/t. Washing loss is about 6% of chemicals. The weak black liquor conc. 8%. The black liquor is filtrated on a vibrating screen 100 mesh. The fines content in filtered B.L. is about 150 ppm.

The evaporation battery is 6 effect 7 body (No.1 is double) LTV plus a forced circulation LTV. Each LTV body has 530 m^2 surface, the FC has 365 m^2. The evaporated water is 48 t/h. The inlet to FC body is 38% conc., outlet conc. 44-45% (8m^3/h). The steam is flowing 1-2-3-4-5, W.B.L. to 5 effect returning from 6 to 4-3-2-1 and FC. The steam economy is 4.2 t of water/1t of steam. The evaporator is cleaned once per month with 200 h pressure water. The evaporator battery was manufactured by Swetha Engg. Madras.

The semi-concentrated B.L. is further concentrated on a cascade direct contact evaporator to 60-62% conc. of dry solids. The heat value (HHV) of the B.L. solids is about 3,000 kcal/kg. Silica in B.L. solids is 2.25%. Ash content 32%, organics 68%.

The recovery boiler is of AHLSTROM (single drum) typ, 2.58x2.58m, height 22 m. The temperature of primary and secondary air 150-150°C. of B.L. 118°C. The boiler has two oscilating guns at 5.7m height. The recovery boiler is designed for 110 TDS/day, but the capacity of the pulp mill is lower. A second wood-bamboo pulp mill is under construction. The recovery is working intermittently-90% of total time. The boiler has an electroprecipitator. The sodium losses are 2%.

The boiler is generating 8-9 t steam/h (max 10 t/h) 40 bar, 405°C. The steam generation is 2.4 t steam/1t B.L. solids, the boiler has 10 sootblowers operating 1.5-2 hrs/day consuming about 4 t/h steam. This is not too much in percentage of generated steam (total steam 240 t/day), but at time of sootblowing causes problems.

The steam is used for electricity co-generation. The turbine has 10 bar extraction (25% of total) and 4 bar back pressure (75% of total).

Recausticizing is from Hindustan Don Oliver. Causticity is 85%, causticizing efficiency 84%. Loss of NaOH is 2.5% (lime mud 1.5%, grit from slaker 10%). Lime purity is CaO is 72% (average), silica content in lime 1.6-2.1%, CaO consumption about 1.2 t/t NaOH. Lime mud conc. is about 50%, silica content 6.82%.

Total chemical recovery is about 88%. Energy consumption of recovery system is about 300 kWh.

Satpuda pulp and paper mill

The Satpuda pulp mill is manufacturing 55 BDMT / day unbleached and 48 BDMT of bleached pulp per day from bagasse after moist and wet depithing in vertical depithers. Dryness after wet depithing is about 15-20%.

The continuous SUND-DEFIBRATOR type digester has one horizontal tube (1.1 m dia, 8.5 m length). The digester has cold blow. The chemical charge is 16-17% NaOH, cooking temperature 170-175°C, 15 min.. The unbleached yield is 50%, permanganate K number 9 (about Kappa No.14).

The unbleached pulp is washed on 3 stage vacuum drum washer Hindustan Dorr-Oliver 8'x12'. The dilution factor is 3-4 m^3/t of pulp. The estimated washing efficiency is about 87-90%. The weak black liquor conc. is 9-10% and is filtered on a vibrating screen 100 mesh.

The chemical recovery system was supplied and commissioned in 1993 by TMT (India) LTD., Hyderabad. The evaporators are of LTV raising film type five effects and two forced circulation (FC) LTV effects. The heating surfaces are 245, 245, 295, 295, 295 and two $65m^2$ for FC body. The inlet conc. of weak black liquor is 9.5%, outlet 45% solids. The evaporated water is 22.5 t/hour, steam economy about 3.8 t water/t of steam. The heat value of B.L. (HHV) is about 3,000-3,200 kcal/kg.

The black liquor dry solids are 65 t/day. The recovery boiler is TMT'S own construction with two drums, membrane walls. The furnace zone is clad with replaceable refractory blocks up to the spray gun level (5m above hearth level). The furnace cross section is without refractory 2.54 x 2.34 m with refractory approx. 2.3 x 2.1m. The total height from hearth level is 23 m, from ground level 25 m. The boiler is without a superheater and economiser. the steam pressure is 16 bar (about 200°C). the recovery boiler has a direct contact cyclone evaporator and a Venturi scrubber. The final B.L. conc. is 54-56%.

The recovery boiler is operated without auxiliary fuel except of starting period. The boiler can be operated in a wide range of capacity.

The causticizing system consists of a slaker, rake classifier, 3 causticizers, white liquor clarifier, primary and secondary mud washer and vacuum filter. The capacity is 130 m^3 of white liquor at 100 g/l TTA as NaOH. The lime purity is 60-65% (3.5% MgO, 1.3% silica). Causticizing efficiency is about 80%. Lime consumption about 1.5 t/t NaOH. Causticizing lors is about 82-85% (without washing). Total chemical recovery efficiency including washing is estimated 74-76%. Data are not reliable.

DESCRIPTION OF CHEMICAL RECOVERY IN SOME BAGASSE BASED MILLS
SOUTH AMERICA

KIMBERLEY CLARKE MILL (115,000 BDMT of pulp/a)

The Chemical recovery plant at Kimberley Clarke Mill consists of two streets of multiple effect evaporators, one conventional soda recovery boiler of the B&W design, one Copeland reactor and a causticizing plant of Kimtech design.

The weak black liquor from both streets of the brown stock washing plant are screened on two separate Maloney filters with SS filter cloth (100 mesh) to remove the fibre carried over with the black liquor to the chemical recovery system. No exact figures could be collected at the mill regarding fibre content on the weak black liquor. However, extreme importance is given for the function of these filters, since by practice it has been observed that the utilization of the evaporation plant drops down considerably when these filters are not in operation. These filters are located at the pulp mill. The concentration of weak black liquor from stock washing is around 8.5 to 9% and the volume of weak black liquor is around 11-12 m^3 per t of pulp. The black liquor dry solids per t of pulp is around 1.1 t and the calorific value of the liquor is about 11.5 MJ/kg.

There are two streets of multiple effect evaporators of Svenson design. The first street is a long tube quintuple effect evaporator which includes a concentrator. Weak black liquor fed at 9% is concentrated to 21% in the quadruple effect and then to 36% in the concentrator. Steam economy is estimated as 3.6. The silica in the weak black liquor is around 2-3% and the problem of scaling in the evaporator increases with the concentration of black liquor. The second street of evaporator feeds the black liquor required for the Copeland reactor. The second street is a quadruple effect log tube vertical evaporator with forced circulation in all effects. Weak black liquor fed at 9% concentration is concentrated to 20% solids in this street.

Recovery boiler

Semiconcentrated black liquor from first street is sent to the B&W recovery boiler. This B&W boiler is designed for firing 125 tons of dry solids per day. The boiler consists of a cyclone evaporator and an electrostatic precipitator. Black Liquor is concentrated in the cyclone evaporator is fired in the boiler through six fixed guns, atomized by steam. Unlike a conventional kraft liquor sprayer the liquor burner is similar in design to a conventional oil burner with pin holes on the periphery for the atomizing steam. The soda black liquor does not form a char bed and the combustion takes place mainly when the liquor is under suspension. The liquor is sprayed at a pressure of about 0.3-0.25 MPa at 110°C. The liquor spray guns point downwards at an angle of 50 and the atomized liquor spray dehydrates while in suspension. Forced draft fans provide the requisite amount air for combustion through primary and secondary air ports with 4-5% excess air.

The essential features of the recovery boiler are generally similar to any conventional recovery boiler. Sulphur is not present in the system and hence there is no reduction atmosphere required in the recovery furnace. The make up chemical is sodium carbonate and is added at the dissolving tank where the smelt from boiler is dissolved in weak white liquor from the causticizing plant. The boiler hopper ash well as the ash from the electrostatic precipitator are added at the dissolving tank. The smelt flow from the boiler is smooth.

Copeland fluid bed reactor

The semi-concentrated black liquor from the evaporation plant from at the about 20% concentration is sent to the Copeland reactor. Copeland reactor is a fluidized bed liquor burning system. The main advantage of this reactor appears to the fact that the maximum concentration of black liquor to be handled in the only 35%. This is a great advantage especially for bagasse liquor which has high viscosity.

The Copeland reactor system has a Venturi scrubber for secondary evaporation and semi-concentrated black liquor at 20% is used at the Venturi to scrub the flue gas. The liquor concentration consequently gets increased to 35%. The concentrated liquor is pumped to the specially designed liquid spray gun located on top of the reactor which injects the liquor with the help of air into the upper free space of the fluidized bed reactor, know as "free board". The liquor is concentrated as it falls downward to the bed. The flue gas temperature is around 660°C.

The dry solids flow downwards onto the fluidized bed. The fluidized bed consists mainly of granular inorganic residue. The sodium hydroxide is converted into sodium carbonate pellets and is withdrawn from the side of the reactor. These pellets fall directly into the dissolver and are mixed with the weak white liquor. The green liquor so formed in the dissolver is sent to the causticizing plant.

The bed in the reactor is maintained as a fluidized bed by the forced draft of air sent into the reactor from the bottom of the unit. The fan is run by a steam turbine for proper control of the air flow. The delivery pressure of the fan is normally maintained at 41 - 48 kPa. This however depends on the characteristics of the fluidised bed. Flue gas leaving the Copeland reactor is stripped of entrained dust particles that are collected in the cyclone and returned back to the bed of the reactor. The flue gas from cyclone enters the Venturi scrubber where the semi-concentrated black liquor at 20% is injected through nozzles. The liquor is concentrated to about 35% solids ba the heat transferred from the flue gas. Any liquor that is entrained in the flue gas is stripped in the separator and the gas is discharged to the atmosphere through the chimney.

During start up to the Copeland reactor after a prolonged shut (cold shut) the air to be sent for the fluidisation is heated up in gas fired air preheater to about 525°C. Once the bed reaches this temperature granular char-coal is injected into the reactor bed. Combustion of char-coal commences at about 355°C and the temperature of the reactor rises up to 635°C. At this temperature injection of the semi-concentrated black liquor from the top of the reactor is started. The Copeland rector is able to run for about 3 months continuously without any stoppage. Accordingly to mill executives the performance of the reactor is satisfactory without any major breakdowns. No specific economics of the Copeland rector as compared with the recovery boiler has made by the mill. However, the main reason for the preference for the Copeland reactor appears to be its low initial investment.

PROPAL MILL, COLOMBIA (260 BDMT of pulp/day)

Evaporation Plant

The black liquor concentration from the washing plant is 8.5-9% solids and is concentrated to about 45% in a quintuple effect evaporator of the Svenson design. The evaporation plant is equipped with a forced circulation evaporator of single pass type. The plant has an evaporation capacity of 153.6 m^3 of water per hour with a steam economy of 4.0. All evaporator have SS tubes od size 2". The vacuum system consists of a surface condenser and a two-stage steam jet ejector unit.

The main problem in the operation of the evaporation plant appears to be scaling of the evaporator tubes especially in first and second effect evaporator where the liquor concentration is high. Boiling out with water is carried out once a week and a caustic wash is given once in two weeks. Every year hydrofluric acid cleaning is also carried out. The main reasons attributed to the scaling in the evaporator tubes are the silica concentration (3 to 5%) and the fiber content (0.012%) in the black liquor.

Reportedly scaling in the first and second effect is high due to high viscosity of black liquor at higher concentrations and the viscosity of black liquor at higher concentrations and the viscosity is controlled by maintaining 6-8 gpl free alkali as NaOH in the black liquor received from the washing plant.

Recovery boiler

The recovery boiler is an Ahlstrom unit of the Combustion Engineering type with a rated capacity of 365 t of black liquor solids/day. The boiler is equipped with a two drum cascade evaporator which runs at about 5.5 RPM and an electrostatic precipitator od the dry bottom type. The boiler produces 54 t/h steam at 4.5 MPa and 400°C. The concentrated black liquor at 45% solids from the evaporation plant is supplied to the two-drum cascade evaporator in the recovery boiler unit. The temperature of liquor entering cascade is around 80°C. In the cascade evaporator the concentration of the black liquor is increased to 60% by the heat transferred from the flue gas. The 60% liquor is then taken to the mixing tank through the rotary screen in the cascade to avoid lumps from entering the mixing tank. The concentrated liquor is then pumped (by a gear pump) to the boiler through a direct steam heater. the black liquor at a temperature of 120°C is sprayed by means of 6 fixed guns. The guns point downwards at an angle of 50. The black liquor is fired into to the boiler by atomising with steam. the spray pressure is maintained at 0.35 MPa atm. The spray guns appear similar to conventional oil burners. The recovered chemicals fall into the dissolving tank through two smelt spouts which are cooled with boiler feedwater.

The boiler is equipment with primary, secondary and tertiary air registers and the air is supplied by a FD fan driven by a steam turbine. The distribution of the air between the primary, secondary and tertiary is estimated as 20, 60 and 20%. Normally 4% excess oxygen is maintained in the flue gas leaving the economiser, for proper combustion control. The boiler is equipped with 12 electrically operated automatic retractable soot blowers for the superheaters and boiler, and three soot blowers for the economiser. The ash collected in the electrostatic precipitator is mixed with water in a tank where sodium carbonate make up is also added. The liquor is then pumped to the dissolver.

The overall chemical recovery is estimated at 88% and the 12% chemical loss is distributed as given below:

Pulp mill (washing plant & digester)	3.5 to 4.0%
Multiple effect evaporators, recovery boiler	4.0 to 4.5%
Recausticizing plant (Slaker grits and lime sludge)	3.5 to 4.0%

Bagasse black liquor recovery in LEDESMA S.A.A.F. Mill, Argentina (150 BDMT/day)

The depithed bagasse is stored using the Ritter wet system and is cooked by the soda process in two PANDIA digesters. The Kappa no. of washed pulp is 14. The bagasse is washed on three IMPCO countercurrent vacuum washers of 2.9 m dia and 4.9 m face (44.6m²). At a nominal capacity of both lines 150 BDMT per day the loading of the washers is 3.36 BDMT/m², which is considering lower than for pulp. the weak black liquor is filtered on a inclined (45%). DSM Dorr-Oliver screens equipped with mesh number 80. The concentration of fines in the weak black liquor is reduced from 85 mg/l to 45 mg/l. The solid concentration of the weak black liquor is 8.13% (average), the ash content in solids is 38.7% and silica as SiO_2 in solids 1.2%.

The black liquor is evaporated on a five-effect vertical long tube evaporator (tubes dia 50 mm, length 7.2 m). The average heat transmission coefficient is 976 kcal/m².h.°C (4,080 kJ/m².h.°C). The outlet conc. is 40%. The steam consumption per kg of evaporated water is 0.22 kg and 2.5 kg steam per kg of total dry pulp.

Scaling with silica is a serious problem especially in I and II effect. the outlet concentration of B.L. is 38 % with clean tubes but 29 % only with scaled tubes. The silica scale is difficult to remove. the practice is boiling two hours with a 20% solution of sodium acid sulphate (bisulphate) followed by mechanical cleaning. Calcium carbonate (mainly III but also IV and V effect) is removed with 4% hydrochloride acid with inhibitor. Concentration of B.L. at evaporator outlet should not be higher than 40% in order to avoid serious silica scaling. the B.L. is further concentrated on a cascade direct evaporator to 65% dry solids content. due to viscosity of bagasse black liquor the cascade evaporator drive is over-sized.

The recovery boiler is a Babcock/Wilcox unit with a capacity to burn 156 tons of dry solids per day corresponding to 1,150 kg of dry solids per BDMT of pulp. The heating value of solids is 3,294 Kcal/kg (13.7 MJ/kg). The B.L. is heated with direct steam to 105°C decreasing conc. from 65% to 62%. The pressure at the B.L. Burners is 5 bar (0.5 MPa). The air distribution is 65% for primary and 35% for secondary air (0% tertiary air). Gas (about 30 m³ per hour) is used as auxiliary fuel (4.6 m³ per ton dry solids). The steam production at nominal capacity is 20.7 t/h at 426°C and 45 bar (4.5 MPa). At a capacity of 100 BDMT of pulp the production of steam is 3.69 t per BDMT of pulp.

The green liquor is causticized with lime and the lime reburned. Due to high silica content the limestone make up is as high as 17% as a part of the mud has to be purged to avoid a too high silica increase. Only 95% of the sodium silicate is causticized. The limestone has a silica content 1.7%.

The total alkali recovery is 84.80%. The chemical loss in washing is 8.4% in evaporators are recovery boiler 3.12% and losses in recausticizing 3.67 %.

STRAW PULP MILL OF THE DUNAPACK DUNAUJVAROS FACTORY, HUNGARY

The pulp mill is producing 28,000 t/year of bleaching pulp from wheat straw. The straw is cleaned mechanically and digested in a PANDIA continuous digester by the kraft (sulphate) method (sulphidity 15-20%).

The chemical charge is 120-140 kg Na_2O (150-180 kg NaOH) per ton of o.d. straw. The concentration of the while liquor is about 60 g/l, 300 l/h are used. The straw consumption is about 7.5 t/h O.D. The specific straw consumption when using high straw is about 2.1-2.3 t O.D. t of pulp. In case of low straw the consumption is higher (up to 2.6-2.7 t/t of pulp). Low straw is considered as inferior raw material.

The liquor to straw O.D. ratio is about 3.1 to 3.4:1. The steam consumption is about 6-7 t/h. The cooking time is 15-18 minutes at 170°C. A special feeding equipment reduces blowbacks practically to zero. The PANDIA digester has two tubes each diameter 1.20 m length 14m.

The pulp is washed countercurrently on a continuous washing line. The first stage is a Rauma Repola pressure filter (3 - stage). The capacity of the filter is about 2.0 t/m²/day. In the next two stages the pulp is washed on SUNDS DPA washing pressure. The first SUNDS PRESS has a dia 900 mm, length 2,140 mm, the second dia 900 mm. length 3,570 mm. Between the washing stages are diffusion chests. The inlet conc. into the presses is 5% conc., outlet 30-32% conc. Each press consists of two rolls covered with a fine wire mesh. In the second washing stage (first SUNDS press) are two presses in parallel. The pulp is washed by 70°C water, which is pumped between the press rolls. The water consumption is 300-500 l/min (18 to 30 m^3/h). The freeness of the washed pulp is 28-32° SR and in case of the low straw 35-36°SR.

The suspended solids concentration in the black liquor is sometimes very high (1,200-5,000 mg/l). The black liquor is filtered on a rotary drum filter and the SS conc. is reduced to 100-200 mg/l. The filter is an own design of the mill. The residual Na_2O in the pulp is 23 Na_2O mg/g of pulp. The capacity of the washing line was designed for 100 t/day, but the real capacity at an acceptable washing efficiency is 70-80 t/day. The Kappa number of the unbleached pulp is about kappa 17. The pulp is bleached by a tree-stage process C-E-H using about 6% Cl in the chlorination stage and 3-4% in the hypo stage. The brightness is 80-82° ISO. The mill has also NSSC pulping of wood.

The weak black liquor from the washing line has a conc. about 10%. The evaporation is 5-stage III-IV-V-II-I. The weak black liquor is entering the III stage and the steam I stage. The evaporators III-IV-V are short tube and I-II long tube with forced circulation. The conc. of the strong B.L. is 54%. Evaporation to higher concentration is not possible due to scaling. Due to silica content good cleaning of evaporator tubes is required. The mill has a good system of cleaning. Every day one effect is cleaned for one shift with condensate 60°C and sometimes with hydrochloric acid. Once a month the tubes are cleaned with high pressure water (200 atm) (WAP equipment). The NSSC black liquor is evaporated separately but sometimes the sulphate and NSSC D.C. liquor is mixed.

The sulphate and NSSC black liquor is incinerated in the same furnace using separate spray guns. The furnace is TAMPELLA with membrane walls and economiser. the strong black liquor is heated to 120°C with direct steam. The designed capacity of the furnace is 9 TDS/h but the practical is 6-7 TDS/h. The heat value of the black liquor solids is 12 MJ/kg. Due to the low concentration of the black liquor auxiliary fuel is permanently used (fuel oil 450 kg/h). The furnace produces 18-30 t/h steam (usually 25-27 t/h) 40 Bar (4 MPa) 420°C.

The green liquor is causticized with lime in a Dorr-Oliver system. The alkali losses in the furnace about 5-7% even if a electrostatic filter is used. The alkali losses in a causticizing are 10-12% as the lime is not returned due to silica B.L. The total losses in recovery are about 17% (recovery 83%). Taking into account washing losses less than 80% of the chemicals are recovered. No data are available about silica content in straw or black liquor.

ANNEX - IV

PROPOSAL FOR FURTHER DEVELOPMENT

PROPOSAL FOR FURTHER DEVELOPMENT

Proposed project title : **Increasing efficiency of black liquor chemical recovery in small pulp mills using non-wood fibrous materials**

Background information : In developing countries more than 50 % of the pulp is manufactured from non-wood raw materials, mainly agricultural residues (bagasse, wheat and rice straw) and various grasses. Most of the mills are of small and medium size (30 to 200 BDMT per day) and are using the alkaline pulping process (soda or kraft). While all wood based pulp mill are incinerating the spent liquor (black liquor) from alkaline pulping most of the small agro-based pulp mills are using the soda process and are draining the black liquor resulting in heavy water pollution and loss of energy intensive caustic soda. In China there are about 6,000 paper mills, most of these are of small or medium size and in 1994 were producing 58 % of total pulp and paper production. Only 81 pulp mills in China have chemical recovery. Out of this are about 20 of small size and are using mainly agro-residues. Only 40 % of about 838,000 tonnes of caustic soda used for pulping was recovered in China in 1994.

In India 40-45 % of pulp is produced in about 230 small and medium size pulp mills. Only two pulp mill had in 1995 chemical recovery and another 4-5 are ordered. The mills are under pressure of environmental limits and increasing caustic soda prices.

Whereas there are several small scale recovery for bagasse and wheat straw black liquor, no chemical recovery is in operation for rice straw black liquor mainly due to problems with rice straw washing and high silica content in black liquor.

The small pulp mill chemical recovery systems in China and India are working with low chemical recovery and thermal efficiency when compared with wood B.L. chemical recovery. The net surplus steam (generated steam minus steam for evaporation of black liquor) is low and in many cases, especially in straw pulp mills the steam generated in the recovery boiler is not sufficient for evaporation of black liquor and steam causticizing. The reasons for this situation are :

- Low black liquor concentration entering the evaporator line (7 to 10 %). The black liquor is diluted by steam condensate from direct steam heating as generally no black liquor is recycled into cooking. Consequently, more steam is used for evaporation than with wood black liquor.
- Low heat transfer coefficient due to high viscosity and scaling of evaporators as agricultural residues black liquor contain or high percentage of silica.
- The black liquor can be concentrated in indirect evaporators due to high viscosity and scaling to 42-45 % only and in direct contact evaporator generally to 52-53 % only. Consequently, less steam is generated when compared with wood black liquor incineration.

Low steam generation and high steam consumption in evaporation is resulting in low steam surplus or even steam deficit.

Development objectives

The long-term objective is to assist developing countries to improve thermal and chemical efficiency of existing recovery systems suitable for small and medium size mill using non-wood raw materials, mainly agricultural residues and grasses.

The immediate objectives are :

- To investigate possibilities of increasing black liquor dry solids concentration entering the evaporation line by decreasing direct heating steam in cooking, testing recycling of black liquor into cooking and by minimizing water for washing of pulp in order to reduce steam consumption for evaporation.
- To increase extraction of organic and inorganic soluble substances in the pulp washing operation to increase chemical recovery efficiency.
- To increase black liquor dissolved solids concentration entering incineration (recovery boiler) in order to increase steam generation. This may be achieved by reducing viscosity of black liquor by modification of cooking and application of new types of falling film evaporators.
- To increase heat transfer coefficient in evaporators by reducing viscosity of black liquor.
- To develop a technology suitable for rice straw black liquor recovery including improved desilication of black liquor.
- To install a demonstration plant in an existing mill in order to test improved chemical recovery and a recovery system suitable for rice straw black liquor.

Proposed organization of the project

The project should be based on co-operation between developing countries, mainly China and India under UNIDO assistance.

The main co-operating Institutions should be the Central Pulp and Paper Research Institute, Saharanpur, India (CPPRI) and the Chinese Pulp and Paper Industry Research Institute, Beijing. Some other Institutions may be included into co-operation, e.g. the Tianjin Institute of Light Industry China. Selected pulp mills and machine manufacturers may be invited to co-operate.

The project activities should be coordinated by a UNIDO Consultant. Detailed working / testing procedures should be prepared in co-operation with the above mentioned Institutions and measurements carried out in mills in order to collect data for optimization of recovery operations. Experiments will be carried out in the above mentioned research Institutions according a detailed and co-ordinated work plan. Optimization of recovery operation will be carried out in co-operation with UNIDO experts.

A demonstration chemical recovery pilot plant may be installed in co-operation with a small pulp mill (e.g. Shiva Paper mill, India). The equipment will be manufactured locally, partly based on foreign engineering. Existing equipment in CPPRI Saharanpur pilot plant may be used.

Characteristics of co-operating Institutes : Both Institutes, in China and India are well equipped and would require only minor instruments and spare parts. Both Institutes are on high technical and scientific level. Some training in special fields may be required.

Proposed UNIDO contribution

International personnel : one Project Coordinator and 2-3 consultants in special fields.

Equipment / engineering :

a) Minor instruments e.g. a Brookfield viscometer for the Beijing Institute. Portable instruments for mill measurement (portable recording thermometers, flow meters, etc.).
   Estimated expenditure : USD 120,000

b) Engineering of the demonstration chemical recovery plant and supply of some sensitive components.
   Estimated expenditure : USD 720,000

Proposed activities

	Proposed activities	**Executing agency / Institution**
1.	Preparation of working / testing procedures.	UNIDO and Institutes
2.	Modification of cooking conditions in order to increase B.L. concentration (e.g. by black liquor recycling. Testing in mill conditions.	Institute, mill
3.	Modification of cooking conditions and B.L. treatment in order to reduce B.L viscosity and verification in mill conditions.	Institutes India, China
4.	Optimization of pulp washing and testing various belt washers in order to improve efficiency and reduce B.L. dilution.	Institutes India, China in co-operation with UNIDO consultant and machine manufacturers
5.	Evaluation of falling film evaporators especially new FF types for evaporation of black liquors to higher concentration and B.L. with high scaling tendency.	Mill in co-operation with Institutes and UNIDO Consultant
6.	Testing of pre-evaporation of black liquor with flash steam from cooking (using e.g. the existing FF evaporator in CPPRI) to reduce live steam consumption.	as above
7.	Investigation of green liquor desilication in order to increase efficiency and B.L. desilication in new installation in India.	Institute with UNIDO consultant.
8.	Engineering of the demonstration chemical recovery plant.	Sub - contractor
9.	Evaluation of demonstration pilot plant	Mill, institute, UNIDO consultant