

Recent developments in chemical recovery processes for small pulp and paper mills.

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Introduction :

The Chemical recovery cycle is a complex series of chemical processes. The three primary functions of a recovery boiler are : 1—to recover and regenerate the pulping chemicals, 2—to burn the organic matter in the **Black liquor (B.L.)**, and thus prevent or minimise pollution and ~~environmental~~ impacts in the plant location and its surroundings, and 3—to ~~recover heat~~ efficiently for ~~production of steam~~ for process use and also for generation of electrical power in most cases.

~~Earlier~~ in our country, recovery plant received a second priority, as it was quite removed from the finished product namely, paper. However, it has received substantial attention during the last decade and now ~~became~~ of the stricter pollution control regulation, requirements and their implementation as well as the rising price of caustic soda.

The chemical recovery cycle has a substantial impact on the economics of pulp and paper production. The cost of a chemical recovery system, which includes evaporators, recovery furnace, causticizers, steam & power generation system, may be as high as 35% of the total plant & equipment cost of a large integrated pulp and paper mill. In the case of a small integrated pulp and paper mill, this ratio(%-age) can be as high as 50% of the total plant and equipment cost. The capital cost of the recovery cycle is thus substantial, both for large and small mills.

In this article, we define our concept of small size as that of a 50 TPD pulp plant. In our country although the number of pulp mills of this size is still not large, this number is going to rise because still smaller mills will have to grow to this size due to environmental as well as economic reasons.

Although Tomlinson recovery system has not undergone any radical changes since the first installation was put up at Canada pulp mill in Windsor, Quebec, Canada during the thirties, there have been impressive and interesting attempts to find alternative methods of recovering the alkali and utilizing the heat from the B.L. organics.

The ~~driving~~ forces for these developments are two fold. They are :

1. Economic pressure :

The limited production capacity of a pulp mill due to limitations of the recovery boiler capacity. The incremental capacity of the recovery recycle would allow increased production of pulp with a level of economy, which the mill can afford. Replacing a recovery boiler is very expensive.

2. Environmental pressure :

Several organic wastes generated in chemical processes have to be destroyed normally by incineration. Some of these sludges are in dilute form and too costly to dewater and then to incinerate. Since incineration is a heat consuming reaction, any recuperative and regenerative heat exchange will eliminate the need for auxiliary fuel to sustain combustion and make the incineration process more cost effective. Developments in this area are opening our minds for more efficient methods of incineration and heat utilization.

Technology vision for alkali recovery of small sizes :

A global scenario of activities in this area indicates

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a spectrum of processes of alkali recovery on a small scale. The various technologies already developed or are being developed, have been grouped into two categories, one of new emerging technologies and the other of currently accepted alternatives. A short description of each of the processes with its advantages and disadvantages and limitations is given. Most of the processes are suitable for alkaline soda pulping process. Fortunately, soda pulping processes, which are sulphur-free and least odour generating, have been adopted for agro-based fibrous raw materials in our country.

New emerging technologies :

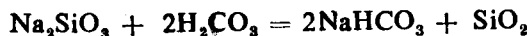
- 1 Wet Cracking Process.
- 2 Chemrec Process.
- 3 Thermo-chemical Conversion Reactor (TCCR) System.
- 4 Supercritical Water Oxidation (SCWO) Process.
- 5 Direct Causticization Process.
- 6 ABC Process.
- 7 Direct Alkali Recovery System (DARS) or the Ferrite Process.

Currently accepted technologies :

- 1 Rotary Drum Roaster.
- 2 Roaster-cum-Smelter.
- 3 Broby Smelter.
- 4 Sulzer-Gedfi Smelter.
- 5 Dry Pyrolysis Process : SCA-Billerud Process.
- 6 Wet Air Oxidation (WAO) Process - Zimmerman Process.
- 7 Copeland Reactor.
- 8 Tomlinson Furnace.

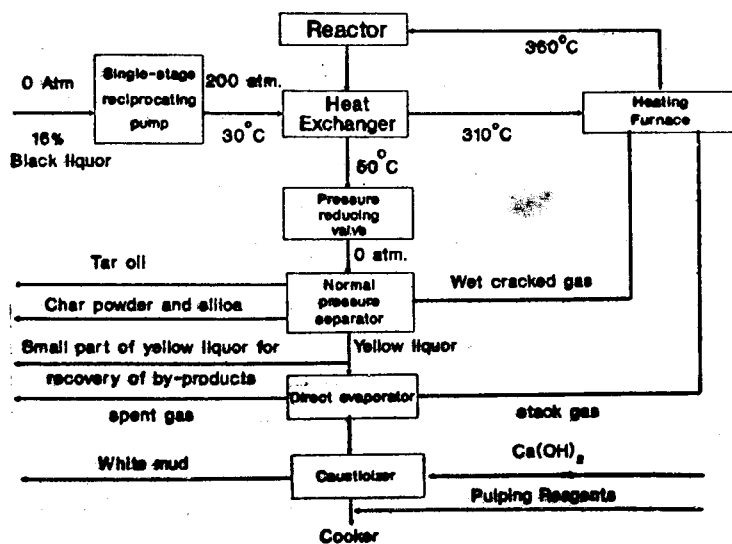
Wet Cracking Process:

In this process dilute B. L. of 16–18% solids is subjected to wet cracking in a reactor at 360–370°C and 190–210 atmosphere for 20–30 minutes in absence of oxygen. Gases, tar oil, yellow liquor containing Na_2CO_3 and NaHCO_3 and a little organics and charred powder are produced. SiO_2 in B. L. precipitates due to presence of CO_2 as follows:



The pH of the yellow liquor is about 8. The yellow liquor is heated for 20 minutes to convert

NaHCO_3 to Na_2CO_3 . Nearly 85% energy to heat the yellow liquor comes from the heat of combustion. A Block diagram (Fig 1), shows the general flow sheet of the wet cracking process. Dil. B.L. is pressurized to 200 atm., heated to 360°C by the combustion of gases before being fed to the reactor. A part of the stack gases goes to a direct contact evaporator to heat the yellow liquor (for conversion of sodium bicarbonate to carbonates). The sodium carbonate is recausticized by lime to sodium hydroxide, which is used as the cooking liquor.



WET CRACKING PROCESS

FIG. 1

The process claims to achieve the following :

	per tonne of B. L. organics
1. Yield of wet cracked gas	120–130 m ³
Gas Composition	%
CO ₂	30-35
CH ₄	12-17
C ₂ H ₆	27-32
H ₂	20-24
Calorific value of Gas	: 6500 KCal/Nm ³
2. Charred powder	90-110 Kg
3. Tar oil	100-120 Kg
SiO ₂ removal, %	96-98
COD retention, %	70-80
BOD reduction, %	60-70
Recovery of Na-salts	more than 50%

It is claimed that wet cracking would cost 50% of conventional recovery plant (I). The Chinese have been working on developing this process. However, it is still in the pilot plant stage. The alkali recovery is low. The yellow liquor still contains considerable organic matters.

Chemrec process :

This new alkali recovery process uses dry pyrolysis to generate a gas mixture of CO and H₂. The dilute B.L. is concentrated to a dry solids content 65% or more in a multiple effect evaporation system. Concentrated B.L. is preheated and is sprayed into a refractory lined reactors along with plasma preheated air. Concentrated B.L. is gasified under reducing conditions at around 900°C

The core of this new process is the refractory lined entrained bed reactor, which is ignited by an electric spark in a reducing atmosphere with insufficient air. The B.L. is decomposed in the reaction zone in to a combustible gas mixture containing CO and H₂. The inorganic sodium compounds form melt droplets of Na₂CO₃ in the case of soda B.L. and of a mixture of Na₂CO₃ and Na₂S in the case of kraft B.L.

The melt droplets and the combustible gas mixture are separated in a quench dissolver, in which

they are brought in contact with a cooling liquid. The inorganic sodium compounds dissolve in the liquid and form green liquor which is causticized with lime in the conventional way. The gas mixture leaving the quench dissolver is freed of melts, passes through a spray scrubber for H₂S removal in case of a kraft liquor and is then used as a clean fuel for steam raising in a boiler or for generation of electricity in a gas turbine subsequently burnt in the boiler for steam generation.

This new process has been developed by Kamyr AB and Goetaverken Energy AB, both of which are controlled by the Norwegian company Kvaerner A S.

A pilot plant with a capacity of 4 tonnes per hour of dry B.L. solids equivalent to 20,000 TPY of pulp production, has been set up at the Frövifors Kraft Board mill in Sweden in the middle of 1991. This pilot installation has increased the pulping capacity of the mill, where the recovery boiler was a bottleneck.

A Flow diagram of the pilot plant is given in Fig 2. The strong B.L. is filtered, preheated and then sprayed in very fine particles into the gasifier unit. Plasma preheated air is used as an oxidant. After cooling in the quench dissolver, the gas mixture is washed and cleaned in a venturi scrubber to remove

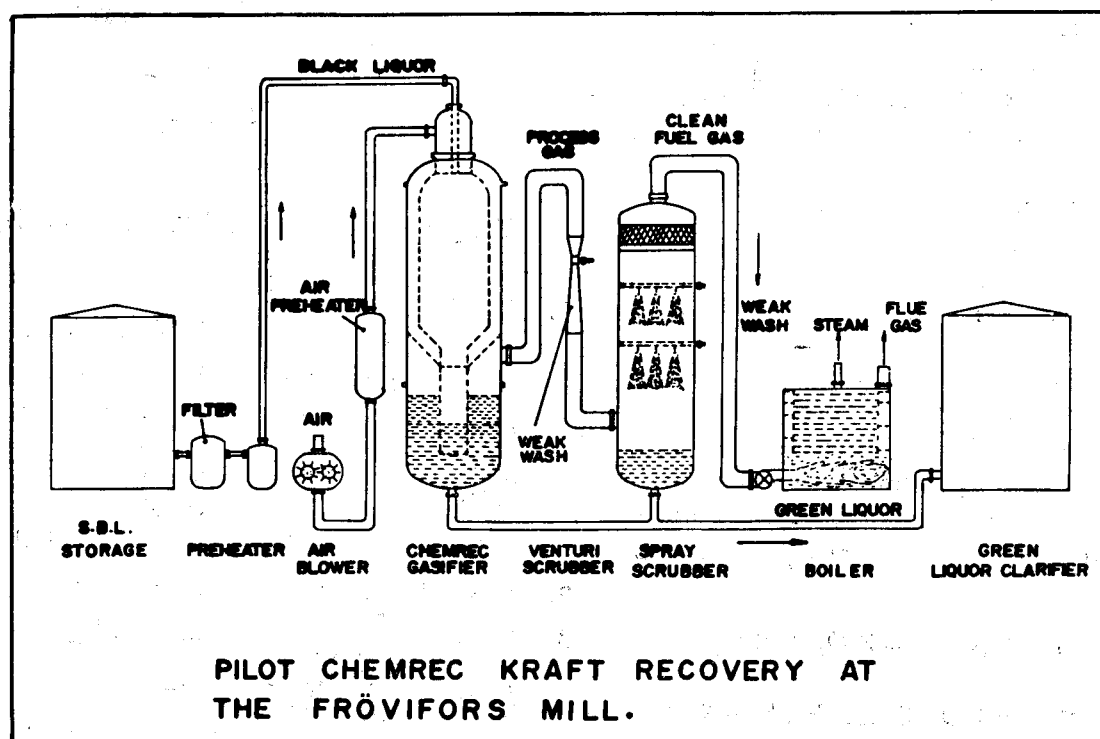


FIG. 2

the H_2S . The clean gas mixture is used as a fuel in a separate boiler to generate steam at 12 bar.

The green liquor solution is drawn from the dissolver and the scrubber and sent to the mill's green liquor system. The pilot plant gasifier operates at nearly atmosphere pressure.

This technology can be varied in a number of ways from low capacity atmosphere air blown system to pressurized air or oxygen blows systems with downstream gas. The gas can be used in a gas turbine for power generation and subsequently in a boiler and turbine for steam and power generation. Thus compared to conventional recovery process, where only steam is generated, this system can yield much higher levels of electric power. Here energy is recovered as fuel gas electric power and steam in a way that meets the needs of the mill. It has therefore better flexibility

with respect to energy usage. A Schematic diagram of Chemrec recovery process with combined cycle of power and steam generation is in Fig 3 (2).

Advantages of the chemrec process :

The advantages of this process are :

1. No risk of smelt-water explosions :

There is no smelt accumulation in the system. The molten inorganics droplets are quenched at the gasifier exist in the dissolver, thus avoiding any risk of smelt water explosions. In addition, the reactor and the boiler are separate. Hence smelt and boiler tubes do not come in contact. It is therefore safer.

2. The combustible gas mixture can be used in the combined cycle of gas turbine and the steam boiler.

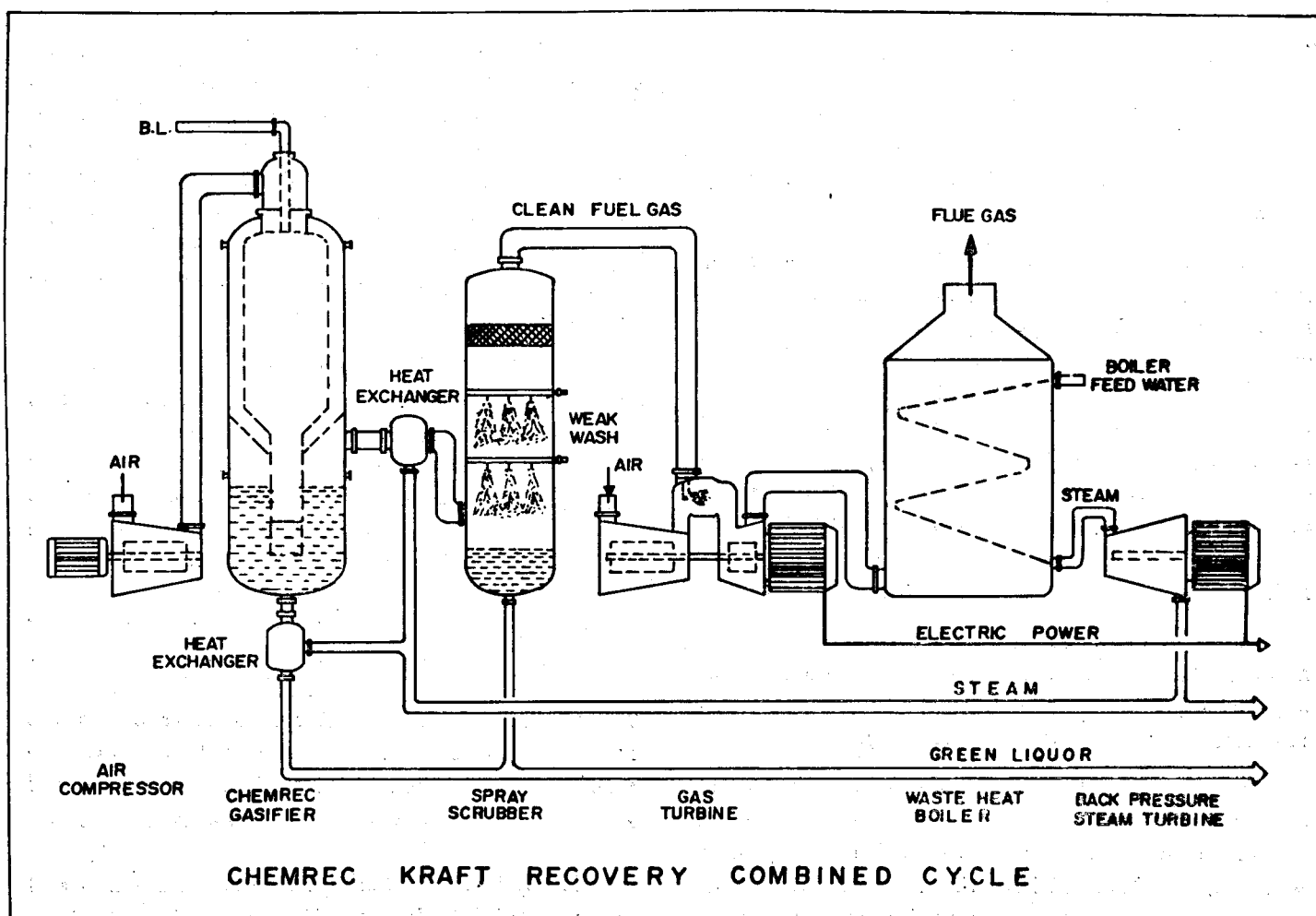


FIG. 3

The electric power yields can be double of conventional steam boiler and turbine cycle. The energy efficiency can be higher.

3. Flexibility in energy generation

Energy can be recovered as fuel gas, electric power and steam in various combinations which permit use that best suits the energy needs of the individual mill.

4. Environmental benefits

As the volume of the flue gas is lower due to controlled air supply, it is cheaper to clean the gases to a given emissions level.

H₂S is removed from the gas mixture in the scrubbers. Further complete oxidation takes place in the gas turbine combustor. Hence sulphurous malodorous gases are non-existent.

5. Compact installation and favourable capital cost investment

The capital cost of the recovery system will be lower than that of conventional Kraft recovery system.

The Plasma reactor replaces the recovery furnace. A Plasma is a luminous gas which has been ionized into positive and negative charge carriers. It releases energy by radiation and heats a medium more efficiently. The new Swedish Company Chemrec, which comprises of Kamyr AB, Goetaverken Energy AB and Kaverne A.S., is exploiting the SKF Plasma technology in the Chemrec process. The new recovery system will be marketed by the Goetaverken Energy AB of Sweden.

Indirect gasification of Black Liquor (MTCI)

Manufacturing and Technology Conversion International (MTCI) Inc, U.S.A have developed a process of indirect gasification of B.L. to produce a high calorific value fuel gas (2000-2500 Kcal/m³).

The gasification takes place in a so named "Thermo chemical Conversion Reactor (TCCR)". It comprises a steam fluidized bed containing heat transfer tubes, where B.L. is fluidized into the reactor. B.L. solids undergo vaporization and pyrolysis reactions. Higher hydrocarbons of the pyrolysis products are steam-crack-

ed to produce low molecular weight products. The fire tubes are immersed with the char formed by gasification. The char is gasified by steam to produce fuel gas with high hydrogen content. The product gas composition (3) is :

50-60% H₂
5-10% CO
20-30% CO₂
2-10% CH₄

The gas has a higher heating value 2000-2500 Kcal/Nm³.

The pyrolysis takes place at lower temperature (530°-630°C) to avoid melting of sodium salts. The sodium carbonate char is taken out of the reactor, dissolved and causticized with lime in the conventional way.

The hot product gas is freed of entrained dust in a water jacket cyclone. Heat is recovered by passing the gas through a heat recovery boiler for steam generation. The gas passes through a wet scrubber for further cleaning of dust and soluble gases. The fuel gas is used for heating the TCCR. The heat of the flue gas is recovered in a waste heat boiler and a Direct contact B.L. evaporator. A simplified Block diagram is shown in Fig. 4(4).

In the MTCI process, pulse combustion heaters are used for indirect heating of the fluidized bed reactor. This pulse combustion technique gives 5-10 times higher heat transfer rates than those of conventional heaters. It also moderates the peak fire-tube wall temperature and prevents smelting of inorganic salts of the B.L.

It is claimed that this system can burn semiconcentrated B.L. without auxiliary support fuel (5). At 65% B.L. solids, the total thermal efficiency is said to be 72% (3). It is claimed that it can generate excess gas for power generation in a gas turbine. It claims to provide a recovery system with low investment cost and a system suitable for small as well as large plants.

The system has a high turn down ratio (2:1) and can use sulphite liquor. H₂S is oxidized to SO₂, which is mixed with Na₂CO₃ to form sulphite liquor.

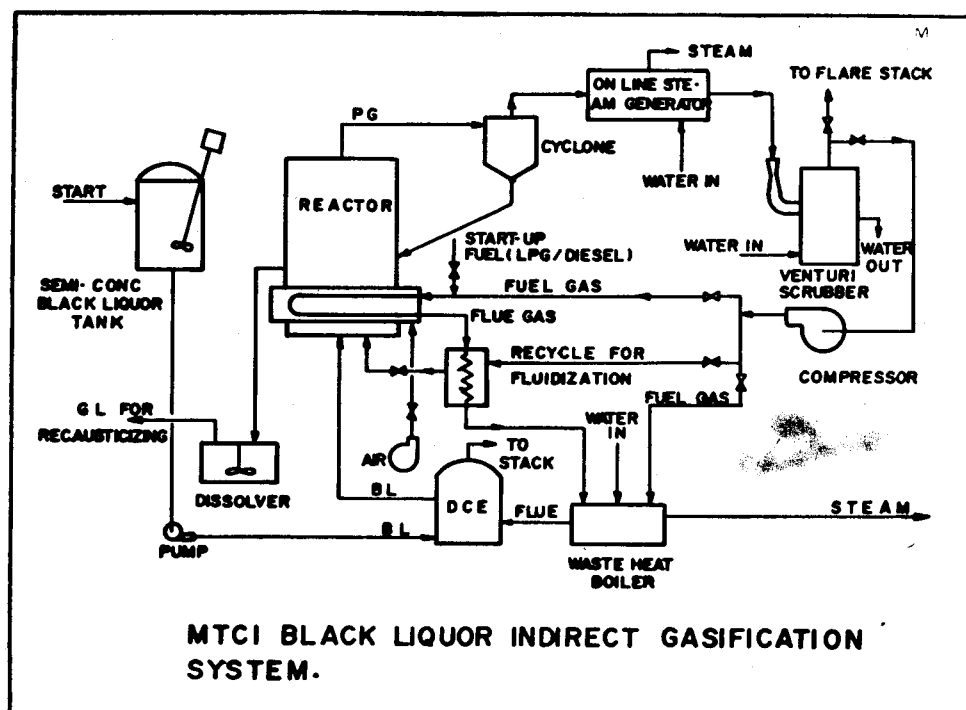


FIG. 4

Two pilot plants for B.L. burning are under installation. They are :

- 1 Seshasayee Paper & Boards Ltd., Erode, (T.N.), INDIA.
- 2 Weyerhaeuser, New Bern, North Carolina, U.S.A.

The pilot plant at Seshasayee Paper & Boards Ltd., India has a capacity to process 500 Kgs. of B.L. solids per hour (4).

The third pilot plant to be installed at a Waste paper based linerboard mill in Canada is to burn 1 T/hr. process rejects of the mill.

A fourth pilot plant is planned to be installed at the Weyerhaeuser Springfield (Oregon, U.S.A.) mill to burn 18 T/hr. coal.

Supercritical Water Oxidation Process (SCWO):

SCWO is a process for oxidising organic wastes, and converting them to CO_2 and inorganic substances. It is similar to wet air oxidation process (Zimpro

process). Here the oxidation is conducted differently. Combustion takes place at a temperature of $400^\circ\text{--}600^\circ\text{C}$ and at a high pressure at 250 atm.

At atmospheric pressure, it is not possible to burn organics at low temperatures ($400^\circ\text{--}600^\circ\text{C}$) without charring. Organics usually char and char burns only at high temperatures ($900\text{--}1000^\circ\text{C}$). Oxidation of organics at lower temperatures is possible at higher pressure and in presence of water which becomes the reaction medium.

Water above 374°C and 218 atm. is a supercritical fluid. In that stage, it becomes a good solvent for organic substances and gases. SCW, also transforms organics to small molecules. These small molecules are readily oxidised by air or oxygen.

Typical features of SCWO process are :

1. B. L. can be fed even at 10% solids, thereby eliminating evaporation.
2. Regenerative heat exchange is used to preheat, the feed and cool the product thereby eliminating

auxiliary fuel to sustain combustion. In the external heat transfer loop circulating fluid picks up heat in the cooler and passes it to the preheater.

3. Nearly 40% of B.L. heat value can be recovered as steam which can be used in the pulp mill.
4. CO_2 can be recovered, which has a good market value and hence can provide enough by-product credit.
5. Liquefaction of CO_2 controls gaseous emissions and this process has better environmental acceptability.
6. Oxidation at 600°C and longer time gives 99% combustion efficiency. It destroys dioxines and chlorinated organics.

Basic steps in SCWO :

A Block diagram is given in Fig. 5. The basic steps are :

1. B.L. is pressurised to 250 atm. Liquid O_2 is also pressurised, heated to room temperature and

mixed with B.L. There are 2 phase, e.g. liquid phase and vapour phase. The weight ratio of B.L. to oxygen is 94 to 6.

2. B.L. and oxygen mix enter the preheater, heated to 400°C . Oxidation starts in the preheater. Under this temperature and pressure liquor phase disappears.
3. From the preheater the mixture, now in vapour phase, enters the insulated reactor, where most of organic matter is oxidised. The peak temperature in the reactor is 600°C .
4. After leaving the insulated reactor the mixture is cooled to room temperature in a heat exchanger. Water vapour condenses and forms a liquid phase. This dissolves the acid gases and inorganics.
5. The liquid is separated from the gases (CO_2 & O_2) in a separator. The system is depressurised. Oxygen is separated from CO_2 in gas phase. CO_2 is liquified and sold. O_2 is recycled.
6. Organic nitrogen compounds do not form NO_x in SCWO. Below 500°C NH_3 is the primary product;

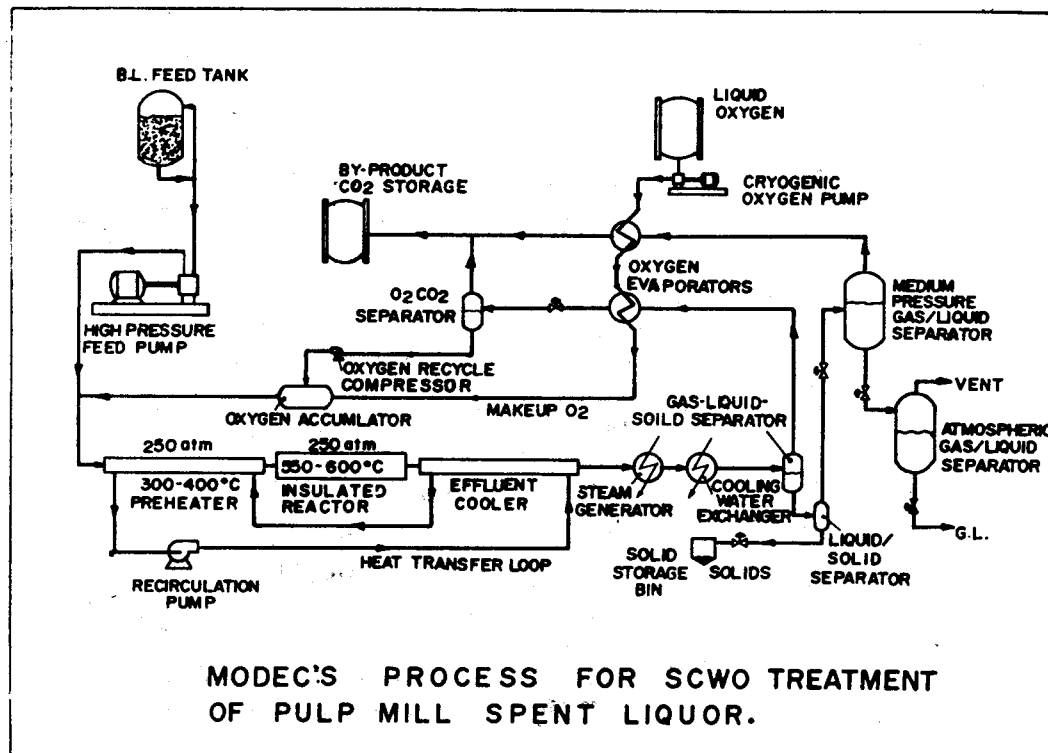


FIG. 5

above 600°C molecular N₂ and nitrous oxides (N₂O) are formed. Hence it has better environmental acceptability.

7. STABILITY OF THE PROCESS

The peak temperature is determined by concentration of waste liquors and degree of preheating. A maximum of 600°C is the limit.

The advantages are :

1. Even dilute B.L. (10% by wt.) can be used as feed to SCWO.
2. Auxiliary fuel is not required even at 10% B.L. concentration. The process is thermally self sustaining if the B.L. with a minimum heating value of 815 KJ/Kg. is fed.
3. Nearly 45% of the calorific value of organic feed can be recovered as steam.
4. It has the best environmental acceptability. There is total absence of malodorous gases and particulate emissions. Destruction of chlorinated organics including dioxines is complete (99.999%) due to total oxidation.
5. The design of preheater, reactor and the coolers (exchangers) are modular. A minimum capacity of 20 TPD solids (equivalent to 10-15 TPD pulp mill capacity) is desirable. For a 100 TPD solids 5 modules can be operated in parallel.
6. It is safer to operate this system. The presence of water in high concentration moderates any possibility of explosions.

This supercritical water oxidation technique of burning waste materials have been developed and patented by Modell Development Corporation of U.S.A. (MODEC) (6, 7). Prior to 1989, SCWO technology was limited to processing of organic wastes without inorganics, as salts would precipitate out in the reactors and clog them. Subsequently MODEC has devised proprietary designs for the components which allow processing wastes such as B.L. without clogging the equipment.

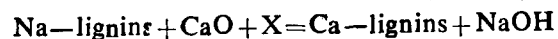
Plan to build a 5 TPD pilot plant is under consideration.

This process is very suitable for processing of waste water treatment sludge. A 100TPD sludge processing demonstration plant is planned to be installed in 1993 (8).

Direct causticization process

A major part of sodium salts in the B.L. is attached to the organic matters, although a very small part exists as a free titrable alkali as well as sodium sulphate.

In a newly developed and patented process, dilute B.L. prior to evaporation is treated with calcium hydroxide along with undisclosed chemicals (polyelectrolyte coagulants) to precipitate lignins and other hemicelluloses. During precipitation, calcium replaces sodium and generates sodium hydroxide according to the reaction.



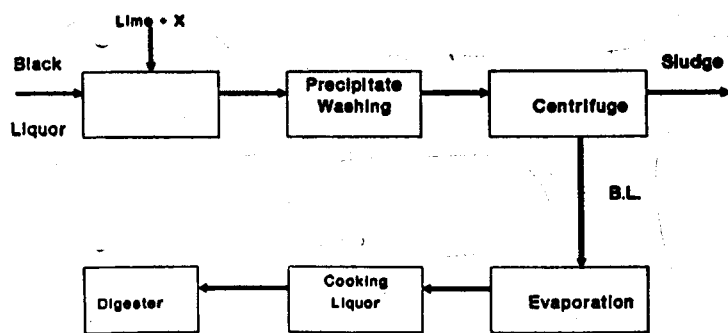
The dilute caustic solution can be concentrated to any desired level of NaOH concentration for use as cooking liquor or otherwise. The precipitate is removed by centrifugation or filtration and washed for improved recovery of sodium hydroxide. Lignin can be recovered and used as a source of fuel. The ash containing calcium oxide can be recycled.

In the bench scale trials, sodium recovery varied between 95% to 99%. The calcium content of the caustic soda solution as less than 10 mg/l. The solids content of the centrifuged precipitate was 30%. In addition, silica present in the B.L. is precipitated along with calcium salts. The yield of organic matter was 95%. (9).

A Block diagram (Fig. 6) gives the various steps involved in the direct causticization process.

The advantages of this unique process are :

1. It is simpler in operation.
2. It is not necessary to concentrate B.L. prior to direct causticization. Dilute B.L. is used as feed.
3. Silica is removed from the cooking cycle through the Ca-organics precipitates.



Direct Causticization Process



FIG. 6

4. Lignin can be used either as fuel or as a source for other lignin products.

However, all work done till today are limited to bench scale trials. Thermax (Pty.) Ltd., owns all rights of this innovation.

ABC recovery process

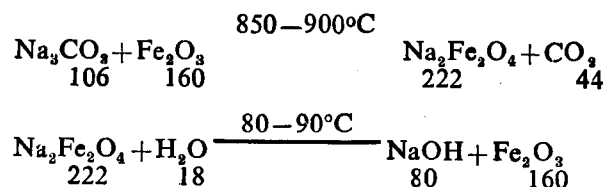
Semi-concentrated B.L. (30-35% solids) is mixed with a solid fuel (in this case organic wastes such as chopper dust of rice husk) and fed to a furnace with movable grate for incineration. Temperature is controlled to avoid smelt formation. The charred and incompletely burnt clinker coming out of the furnace hearth with a movable grate is leached with water. The solution is primarily sodium carbonate and sodium silicate. It is filtered to remove the carbon particles. The green liquor is carbonated to precipitate SiO_2 , which is separated by sedimentation and filtration. The clarified green liquor is causticized lime for production of white liquor. The white liquor concentration is very low. It is claimed that the precipitated silica, has a good market. The mill claims that the process would be economical in view of the high price caustic soda as well as of the recovered silica.

The technology is indigenous and needs considerable developmental work. A pilot plant has been set

up at Amrit Papers in Punjab, which is a division of Amrit Banaspati Company Ltd. (10).

The ferrite process (DARS)

An old patent of Loewing in 1883 describes a novel method of making caustic soda from soda ash according to the following reactions :



Sodium Carbonate and Ferric Oxide are heated to $850-900^\circ\text{C}$, when sodium ferrite is formed. With water the Ferrite forms sodium hydroxide and ferric oxide (solid). The precipitated Ferric oxide is separated from the mother liquor, washed, dried and used again.

In conventional method of causticization of Na_2CO_3 by lime, one follows the reaction



Calcium carbonate is burnt to calcium oxide.

An overall energy balance would show that the ferrite route for making hydroxide from carbonate is more favourable.

The basic scheme of the ferrite recovery process was later on developed by Toyo Pulp Co. of Japan and patented in 1976. Australian Paper Manufacturers Ltd. (APM) got interested in the process and entered into an agreement with Toyo Pulp Co. in 1977.

Various types of techniques and equipment were considered for carrying out the main reaction, namely combustion of organics and the Ferrite formation. The fluidized bed system was finally selected and experimented in a pilot plant, set up in 1980 at Maryvale.

Black liquor of Eucalyptus or pine is concentrated in an evaporator. The concentrated or semiconcentrated black liquor is fired in a fluidized bed reactor which

contains a bed of ferric oxide. Initially, the temperature of the bed materials is raised to the reaction temperature by auxiliary fuel (gas or oil). Black liquor is fired into the reactor. The hot gases leave the reactor through dry dust cyclones and finally stripped off dusts in a wet scrubber. The hot reaction products (mostly Sodium ferrite) are withdrawn through a pipe to a fluidized bed cooler with tubes for water circulation. The cooled sodium Ferrite is decomposed with warm water at 80-90°C. The ferric oxide precipitate is filtered on a horizontal belt filter and reused again. The filtrate is the concentrated sodium hydroxide.

Australian pilot plant experience showed that the process is very stable over a wide range of feed conditions of black liquor. An excess Ferric oxide above stoichiometric ratio is needed for optimum reaction.

The concentration of sodium hydroxide was between 120-200 g/l with a causticity of 90-95% compared with a normal white liquor conc. of 100 g/l NaOH with 80% causticity. Higher concentration of NaOH in the digester has many advantages. One could feed green fibrous raw materials in the digester and still maintain a given chip/liquor bath ratio. For the same bath ratio, one can recirculate more black liquor and hence increase the concentration of black liquor fed to evaporators.

Higher causticity of white liquor means less dead load of Na_2CO_3 in the system and hence less lime requirement for recausticizing with lime in a conventional recovery system.

The hot flue gases escaping from the reactor is a potential source of heat energy. The gases leaving at 800 °C can be utilized for generation of steam and electricity.

The thermal efficiency (enthalpy of gases for steam generation) of any recovery system depends on the dryness of black liquor fed to the furnace. Higher the dryness, higher is the thermal efficiency. For the same dryness of black liquor feed, the ferrite process is almost as good as the conventional process.

The Ferrite Process can stand wide fluctuations in Black liquor solids content. Even black liquor with as low as 40% T.S. can be burnt in the reactor, provided sufficient heat is available.

One major advantage is the absence of smelt in the system. The process is safe and a foolproof one as far as smelt-water explosions are concerned

Central Pulp and Paper Research Institute (CPPRI) at Saharanpur, had been carrying out bench scale trials of the Ferrite Process since 1982 and assessed the DARS Technology of Denmark as an appropriate technology for the Indian situation. (11). A pilot plant supplied by Burmeister and Wain Energi A/s has been installed at CPPRI since 1990. The DARS technology transfer is between CPPRI and DARCELL A/S, which is a new company formed by Fredericia pulp mill and Burmeister and Wain Energi A/S of Denmark.

The pilot plant at CPPRI consists of a fluidized bed reactor and the leaching system. The reactor and the leacher are designed to process 275 Kg/hr. of B.L. solids in a batch operation.

The advantages of the Ferrite Process over the Conventional Process are summarized in the Table-1.

TABLE—1

	Conventional	Ferrite
Explosion possibilities	High	Nil
Concentration of Feed Black Liquor	High (60-65% T.S.)	Moderate (40-65%)
Concentration of NaOH	Moderate (100-120 g/l)	High (120-200 g/l)
Causticity of White Liquor	Moderate (80-85%)	High (over 90%)
Thermal efficiency	Moderate	Moderate
Simplicity of Operation	Moderate	Simple
Operation Cost	Base	Lower
Tolerance to non-process elements	Not good	Good

Where do we stand with DARS

The commercial plant in APPM, Burnie, Australia could not be successfully commissioned due to several design deficiencies and operating problems.

Similarly, the commercial plant in Fredericia Cellulose A/S, Denmark, could not be run continuously probably due to short comings in the solid handling system. Unfortunately the mill could not withstand the heavy burden of investment of US\$ 21 millions at a time of declining pulp prices in the International market. In addition, the state authorities were firm in not relaxing the deadline agreed earlier between the mill and the state authorities. (12).

It is agreed that a lot has to be done to complete debottlenecking the DARS installations both in Australia and Denmark.

General problems of FBC system :

Defluidization :

The fluidized bed in a fluidized reactor consists of sized bed materials of 0.5 to 2.0 mm in diameter and has a static height of 45-75 cm. The fluidized air maintains the bed material in suspension at an expanded height of 70-115 cm. The air/solid mixture takes the characteristics of a fluid. This results in expanded combustion zone, high turbulence, excellent solid to gas contact and high heat transfer within the bed.

Defluidization in a FBC system is a state of very poor non-uniform fluidization. Defluidization can occur due to agglomeration of bed materials. The density of the bed materials is very critical in ensuring a good dancing fluidization. Agglomeration is avoided by controlling the bed temperature, B.L. feed rate in the reactor and the Fe/Na ratio. The minimum ratio of 1.2/I is essential to prevent defluidization (13).

Agglomeration :

In both Australian and Denmark lump formation was noticed. The lump formation was noticed in the centre of the bed in the Australian mill, where B.L. is fed from the side of the furnace wall. Lump formation occurs usually while operating at high temperature at the centre of the bed of the reactor is higher than at the walls in a fluid bed reactor. This could be a reason for lump formation.

Formation of lumps also occur on the walls of the cylindrical reactor. The velocity of particles is higher towards the centre than near the walls. If the particles

are sticky, lumps begin to form in this region. Lump formation naturally reduces the continuous run and increases shut downs and maintenance problems.

Particulate emissions :

A problem with all fluidized bed combustion (FBC) system is the generation and emission of solid particles. Particle size of bed materials is reduced due to the rubbing of particles against each other during the fluidization process. Fine particles escape along with the flue gas from the reactor.

There is always an optimum particle size distribution of the bed materials of a given density for the best fluidization (fluidization with low air pressure drop) as well as for providing most optimum surface area for the reaction to take place in the case of DARS FBC. The particle size should range from 0.5-2.0 mm in diameter.

In a continuous run of 110 hours in a Japanese DARS-FBC pilot plant of capacity equivalent to 10 tpd of pulp production, nearly 36% of bed material escaped the reactor; 13% of dusts based on original bed material were too fine for recycling. (13) The iron ore used as bed material was obtained by palletizing pulverized iron ore (compacting granulation process.)

In order to recover the solid particles, multicyclones and enlarged electrostatic filters must be used not only to increase the recovery efficiency, but also to reduce the particulate emissions and hence its environmental impact. The very fine fractions (mud like in appearance) are difficult to handle in the following step of leaching and must be thrown out as waste. This percentage may be as high as 15-20%.

Accumulation of nonprocess elements, particularly silica in silica-rich non-woody pulping spent liquor :

In many fibrous raw materials, there are many elements present which do not contribute positively to the alkali recovery process. They are Si, K, S and Cl. Higher concentration of these non-process elements is detrimental to the recovery process.

Volatile chlorides are vaporized and condense on the surface of dust. Finer the dust, higher is the chlo-

ride content. Since the finest dust particles must be discarded, chloride accumulation can be prevented in the recovery system. A small portion of sodium chloride also leaves with the Ferrite, which can be purged through cold leaching of Ferrite preceeding the hot leaching system.

Non-wood plant fibres contain a little of sulphur. It is oxidized to alkali sulphates in the reactor and leaves with the Ferrite. Cold leaching can remove the sulphate. The sulphate level has to be controlled in the system to favourably help agglomeration process.

Potassium is present in the plant fibres and is probably not detrimental.

Silica content in many of the commonly used non-wood plant fibre raw materials is considerable particularly in rice and wheat straw.

If its concentration is controlled, SiO_2 will not interfere in the Ferrite process except becoming a dead load.

Pretreatment of non-wood plant fibres by washing (wet cleaning) or dry cleaning is essential to reduce silica concentration. Moreover, desilication of B.L. is a must for alkali recovery process whether conventional or DARS.

What next with DARS ?

Batch pilot plant trials at CPPRI has shown that DARS plant of FBC type can be self sustaining in combustion without auxiliary support fuel even while burning a straw/bagasse B.L. with a concentration of approximately 50%. Auxiliary fuel is required only during start-up.

As mentioned earlier, emission of dusts is a common problem with all FBC systems. It is controlled through multicyclones and ESP as well as scrubbers. A lot of experience is available world-wide to burn low calorific value wet solids in the FBC systems with waste heat boilers designed for high dust loading bare-tube hanging heat exchanger surfaces, which are easy to clean and sweep.

At this stage of development of DARS one would be quite justified to suggest the simple FBC incineration without the waste heat recovery boiler inspite of

low economic returns as a result of partial recovery of heat. It would also reduce the capital cost and risk element of high capital cost considerably and at the same time allow the industry to gain experience of the simplified DARS process and probably look for solutions to any unknown operating problems with non-wood B.L. It is in this context a scheme as shown in Fig. 7 is suggested.

Work and experiments at the Central Pulp and Paper Research Institute (CPPRI) gave a boost to the DARS concept and its application in India. It should now be responsibility of the industry, which should take over to carry on remaining part of the development. Besides, the boiler manufacturing enterprises should shake off their developmental inertia, show interest and cooperate with the industry for further development of the DARS system.

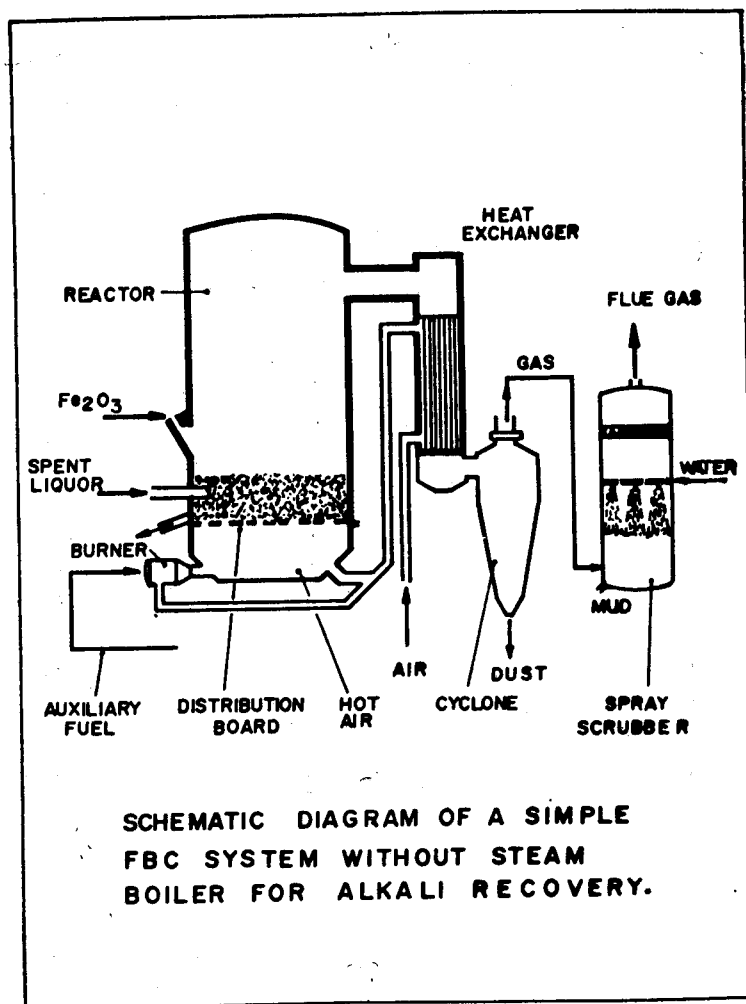


FIG. 7

**TABLE-2. COMPARISON OF VARIOUS ALTERNATE RECOVERY TECHNOLOGIES
WITH CONVENTIONAL TECHNOLOGY.**

	Chemrec	MTCI	SCWO	DARS	Tomilson
Explosion propensity	low	nil	nil	nil	high
Concentration of Feed Black Liquor	high solids 65-80%	semi- concentrated	low solids	semi- concentrated	high solids
Concentration of recovered alkali	moderate	moderate	low	high	moderate
Tolerance to nonprocess elements	not good	good	very good	moderate	not good
Thermal efficiency Applicability to pulping systems	very high kraft, soda	high kraft, soda sulphite	low soda	intermediate soda	high kraft, soda
Simplicity of operation	demanding	demanding	simple	simple	conventional widely practi- ced
Environmental Impact	same as base	favourable	very favour- -able	same as base	base
Operational Flexibility Consistency & Reliability	low good	high not known	high should be good	moderate yet to be established	low excellent
Product mix of energy	fuel gas, steam & electricity	fuel gas, steam & electricity	steam & electricity	steam & electri- city	steam & electricity
Compatability with combin- ed cycle power generation	excellent	excellent	—	—	—
Suitability for small sizes	yes	yes modular	very good modular	good	not-so-good
Capital Cost	marginally lower	marginally lower	not known	marginally lower	base

Comparison of the most promising technologies :

Out of the many new emerging technologies we can short-list the following :

- 1— Chemrec process for wood and bamboo B.L.
- 2— MTCI process for both wood & non-wood B.L.
- 3— Wet oxidation processes like SCWO process for wood & non-wood B.L.
- 4— DARS or ferrite process for wood and non-wood B.L. and
- 5— Conventional Tomlinson type recovery system with desilication step.

Almost all the technologies mentioned above can be used for processing non-wood B.L. for alkali recovery. Each system has its advantages and disadvantages. Many of these new technologies are in the process of development. Experiences in running the pilot plants are limited. There are still many unknown operating parameters which can influence commercialization of these technologies.

However, a general comparison has been attempted and shown in Table—2. Wood based pulp mills can use most of these new technologies for any incremental recovery expansion.

For very viscous and scaling B.L., where it would be desirable to limit the B.L. feed concentration, the DARS, MTCI or SCWO technology would be appropriate.

It may also be mentioned that both SCWO and MTCI can handle B.L., organic sludges of effluent treatment plants and other organic wastes (rejects for example) either separately or in mixture.

From environmental considerations, SCWO technology is the most compatible and probably the safest.

Many of the emerging technologies mentioned above are fascinating, attractive and interesting. Some claim that they are cost effective and are likely to show improvements in environmental features such as lower emissions of particulate solids as well as mal-odorous

gases. However, they are all in various stages of development. A take-off period of 5 years would be necessary to test the efficiency, reliability and consistency of any of these processes.

What do we do then ?

If one could wait, the best would be to watch the progress globally and continue to work locally. In case, if a mill cannot wait and is under pressure of local authorities and the people, the best way is to go for the most conventional recovery technology, i.e. incineration and causticization with lime. It could be a roaster, roaster-smelter or a spray type furnace. Each mill can select a system depending on the capital demand and socio-techno-economic viability. However, all these systems will be more energy negative, i.e. energy must be supplied to the recovery cycle to a much greater extent.

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