Recent developments in chemical recovery-options and opportunities

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ABSTRACT

The recovery of cooking chemical dates back to 1860's. Tomlinson recovery furnace came into existance some time in 1930's. Although significant developments have taken place in process equipments but recovery technology, process wise, remains the same till today. In the past two decades there have been notable developments in the chemical recovery technology. Commercialization of new technologies like wet air oxidation copeland fluid bed reactor and direct alkali recovery system (DARS) has given a hope of having technologies alternate to conventional chemical recovery system Processess like wet cracking, dry pyrolysis, etc are also being studied on bench or pilot plant scale, This paper highlights the status of technologies developed in the past few decades and prospects of their application particularly in small pulp mills in India.

Conventional Chemical Recovery System

Process of recovery, energy and valuable cooking chemicals from kraft black liquor has been practiced for nearly. One hundred years. There have been notable developments in process equipments which has resulted in improved operating conditions and efficiencies. Due to high capital inputs in installing new recovery boilers, industry is looking forward for an alternate pulping process, and subsequent replacement of conventional kraft recovery process. Besides monstrous size and heavy investments conventional recovery has become questionable from the view point of saftly hazards and air pollution. No foresecable changes in liquor burning technology are likely to result in greatly reduced capital requirements & only alternative to overcome the burden of capital intensiveness is to provide means for achieving incremental capacity increases in existing units.

Changing over to soda AQ process from kraft process, has vertually forced the technologists & engineers to look for chemical recovery technologies alternate to conventional technology. Safe operation, minimum impact on the external environment, simple operations, and low capital and operating costs have become requirements for an ideal recovery furnace.

Apprehension are impending on the economic viability and technical feasibility of adoption of conventional chemical recovery technology for smaller size units.

In the last two decades various chemical recovery technologies have emerged and still developments are going on for an alternate recovery systems.

EMERGING TECHNOLOGIES

Among the technologies which have emerged on bench scale, pilot plant and commercial scale can be devided into two catagories, namely—wet methods and dry or high temperature methods.

Wet Methods

In the wet methods the organic components are decomposed under high pressure and high temperature

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either in presence or in absence of air. The cooking chemicals are generated from the mother liquor after separating the decomposed products, by causticization. Some of the processes which have been extensively studied and their present status is described below :

1) **Wet Air Oxidation** : The process is also called as Zimerman process. The basic principle of the process involves wet combustion of preheated black liquor under high pressure. The organic components are oxidised to CO_2 and H_2O. Originally, the method was developed for treatment of pulp mill waste waters. The idea of decomposition of organic substances, by oxidation, conceived, dates back to 1912. Mild oxidation resulted in by-products of industrial application. However, the real value of pulp mill wastes continued to be associated with their inorganic chemical and search for process to regenerate cooking chemicals was started.

The essential features of the WAO process is illustrated in Fig. 1. Air or other oxygen containing gas is brought into intimate contact with an aqueous solution or dispersion of an organic material at an elevated temperature and pressure. The oxidation of organics is an exothermic reaction. The heat of reaction is absorbed by aqueous phase which is partly converted into steam. Normally, WAO plant operates at a pressure range of 2.4 Mpa to 20.7 Mpa wiih corresponding temperatures ranging from 190°C to 327°C. The degree of oxidation required will indicate the operating temperature and pressure. Unlike conventional liquor combustion boilers, WAO can operate with black liquors, having concentration of 6% or even less. However, to reduce the hydraulic size of the WAO system black liquor solids concentration in the range of 12-14% is preferred.

The energy is extracted from reactor vapour phase which consists of primarily CO_2, N_2, O_2 and H_2O. Saturated steam is ptoduced by cooling the reactor vapour on tube side of reboiler while boiling feed water on the shell side.

Among the operating parameters the supply of air and feed of black liquor are important. Feed has to be maintained in such a way so that the resultant products in mother liquor ie. Na_2CO_3 and $NaHCO_3$ do not crystalize.

The input air rate can be expressed as function of the COD of the input liquor.

$$A = \frac{(COD)\ (L')\ (100+E)}{23.15}$$

COD = kg/m^3
L' = Liquor feed rate m^3/hr.
E = Excess air as percentage of theoritical requirement.

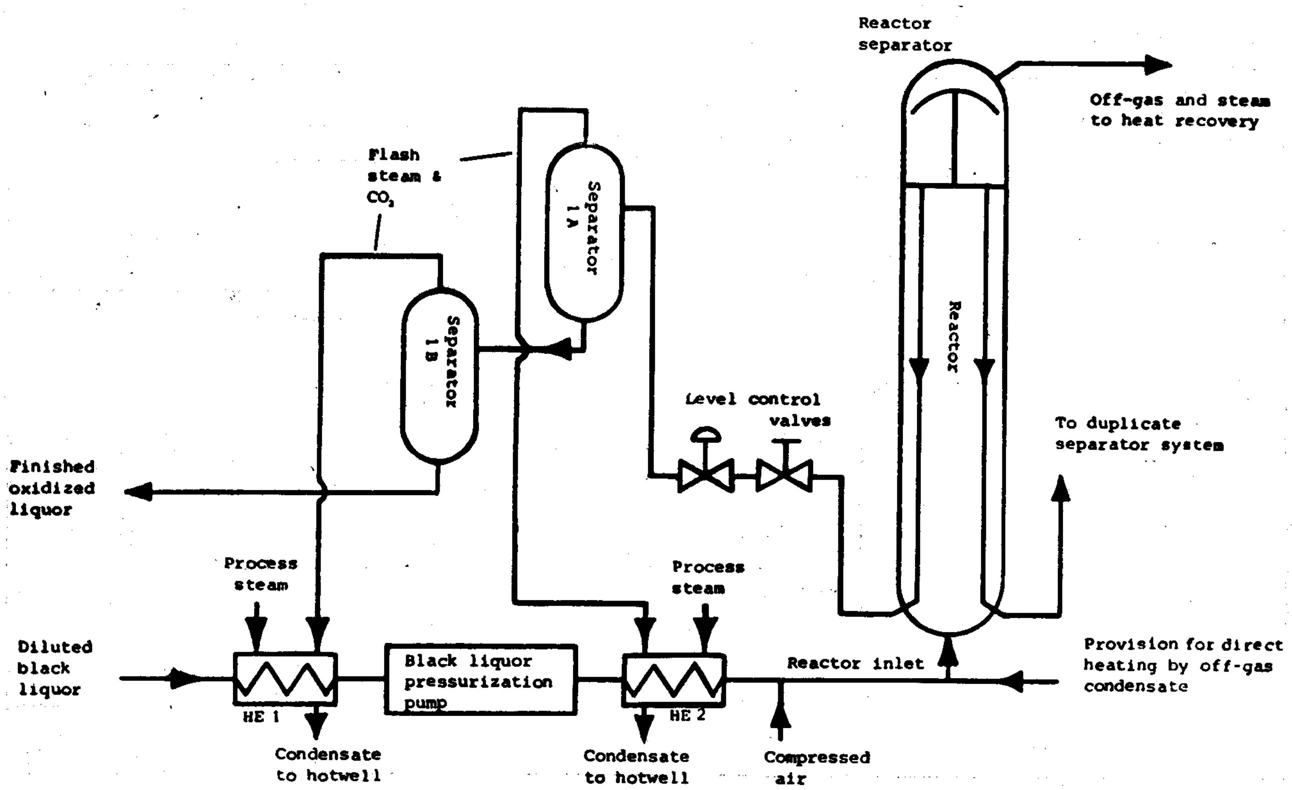

FIG. 1—Simplified Schematic diagram of new WAO plant

Although the energy recovery to the extent of 80% and above can be achieved, but the chemical recovery efficiency is on lower side (60-70%), compared to conventional recovery due to the fact that some of low molecular weight organic acid salts do not oxidise. The advantage of the process is that it is suitable for non-wood fibre spent liquors where silica in black liquor do not affect the efficiency of the process. Further silica gets precipitated in the reactor due to high partial pressure of CO_2 and can be separated easily.

Present Status : The process has been commercialized and more than 100 WAO plants for treatment of different kinds of organic wastes have been designed and installed all over the world. One of the pulp mill in Australia is processing caustic soda from soda black liquor (30 tpd capacity). The advantages are :

- No evoporation
- No air pollution
- No smelting is required.

However, not many installations where designed for black liquor treatment. Though the system appear to be more appropriate for agricultural residue black liquors, but high capital, due to sophisticated material of construction and less flexibility of the process did not attract small pulp mills.

2. Hydropyrolysis Process

The process is a proprietary of St. egic process for recovery of pu'ping chemicals. In hydropyrolysis process black liquor is subjected to a high temperature (700-800°C) while being maintained under pressure in liquid state and in absence of oxygen. Under above conditions the organic components of the black liquor are decomposed to a carbonaceous solid char which is dispersed as slurry in mother liquor. Most of the sulphur and sodium is retained in liquid phase of slurry. The flow sheet of the process is illustrated in Fig. 2. The slurry product from flash separator vessel passes through tube sides of the slur.y cooler, where it is cooled to 100°C. On the shell side of slurry cooler is filtrate which is delivered to caustic room. The char is used in boiler as a fuel. The composition of char and green liquor is given below :—

	Green Liquor	Char	
NaHS	— 16,g/l	Carbon	— 88%
Na_2CO_3	— 46,g/l	Sulphur	— 1,%
$NaHCO_3$	— 87,g/l	Sodium	— 1,%
		Hydrogen	— 3,%

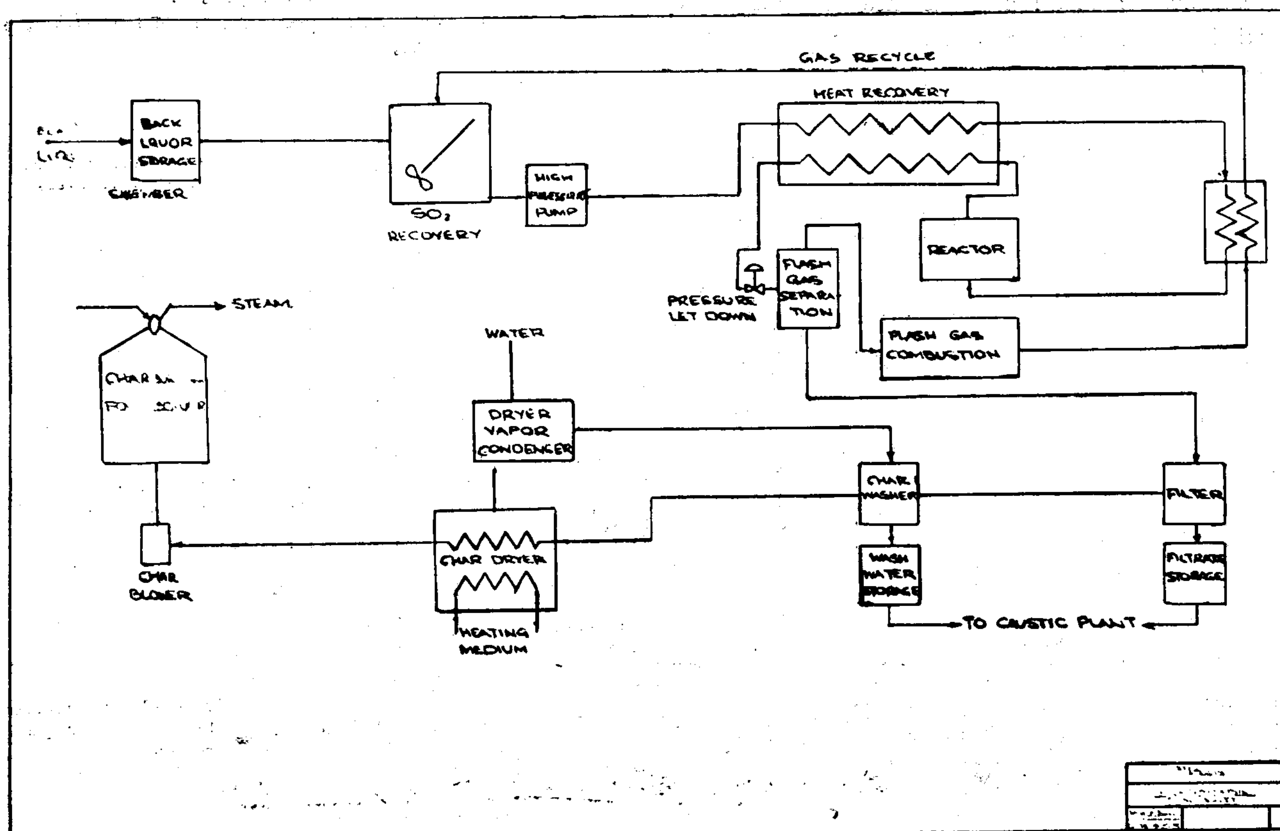

FIG. 2 HYDROPYROLYSIS RECOVERY

Green liquor is causticized by lime. The advantage of the process is that no recovery boiler is used and emission of odorous sulphur compounds are negligible.

Present Status :

Research in this area started in the year 1968 and a 10 tpd p lot plant became operational in 1974 and by June a unit of capacity 330 tpd as designed. The engineering design studies confirmed the commercial application. The cost of the hydropyrolysis system in 1975 was estimated to be of the order of U·S.S. $ 17 900,000 which shows a heavy capital inputs.

3. Wet cracking Pracess :

Wet cracking of black liquor is a recent development by Chinese scientists. The process has been exten;ively studied for processing of straw spent pulping liquor. The basic principle of the process is similar to hydropyrolysis process, except that relatively lower reaction temperatures are maintained in the reactor.

In wet cracking black liquor is reacted under high pressure 200 atmosphere and high temperature 350 °C in absence of oxygen or additives. During this process carbohydrates are coocked, dehydrated and become a char powder. Lignin and other organic matter become wet cracked as gas and tar oil. Sodium silicate is precipitated as silicic acid Wet cracking of black liquor removes 80-95% of organic matter. The char powder and silica is spparated from liquor and the liquor containing Na_2CO_3 and $NaHCO_3$ are sent for lime causticization. The flow sheet of the process is illustrated in Fig. 3. The composition of wet cracked products are given below :—

1. **Wet cracked gas**

   180—220m³/t of organic matter

   Composition

   —CO_2 — 30-35%
   — CH_4 — 12-17%
   — C_2H_6— 27-32%
   — H_2 20-24%
   — Calorific value—6500k. cal/Nm³

2. **Tar oil**

   80-120 kg/t of organic matter

3. **Char Powder-Silica**

   80-120 kg/t black liquor solids.

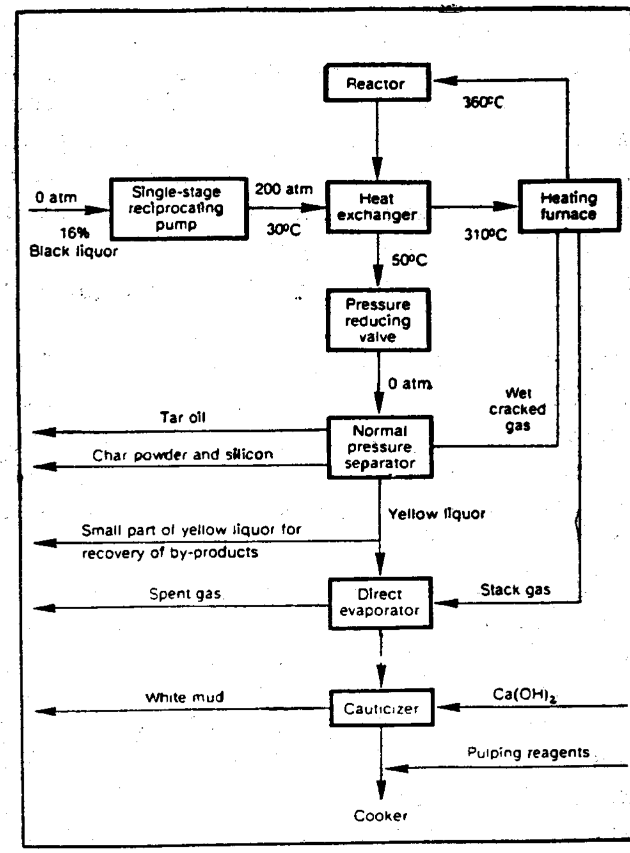

FIG. 3 – WET CRACKING PROCESS.

4. **Yellow liquor**

   Mostly contains sodium bicarbonate and has pH of about 7.

The yellow liquor is boiled for 20 minutes with agitation to convert bicarbonates into carbonates and subsequent reduction in lime requirement. The optimum black liquor concentration is only 16%. The preliminary trials havc indicated thal 85% energy to heat black liquor comes from the heat of reaction.

Present Status :

Research activities on this process were started in the early 80's at Taianjin Institute of Light Industries Tianjin (China). As a result of extensive pilot plant studies a prototype unit of capacity 5000t/year has been designed and is expected to be commissioned soon. Preliminary work out on investments have indicated that the wet cracking system requires ***half the cost of conventional recovery systems.***

Dry (High Temperature) Methods :

Most of the dry methods, including conventional recovery systems involve evaporation of black liquor to a concentration of 60-65% followed by combustion reactor. The reactor, could be, Tomlinson furnace, fluid bed reactor, roaster-smelter or may be a simple roaster. Different technologies which have already been commercialized and also the emerging technologies are discussed below:-

1. Cepeland Fludized Bed System : Compared to conventional recovery furnace, which is relatively complex chemical reactor, operates at much lower temperature (700-800°C), it does not require an expensive water wall construction and pellets of Na_2CO_3 are obtained instead of smelt.

Fig 4 shows the schematic diagram of Copeland fludized bed system used for kraft chemical recovery. The system consists of a single fluid bed reactor, a waste heat boiler, dust removal system. Spent liquor is fired into the top of fluid bed and before liquor strikes the bed, small amount of evaporation takes place. Combustion air is supplied to the fluid bed by means of a blower powered by a single stage back pressure steam turbine with 380 K.Pa, and exhaust steam going to multiple effect evaporator. Air is jetted at a high velocity into the bed through a plurality of nozzles attached to the grid. Dust collected in the flue gas is collected and returned to fluid bed.

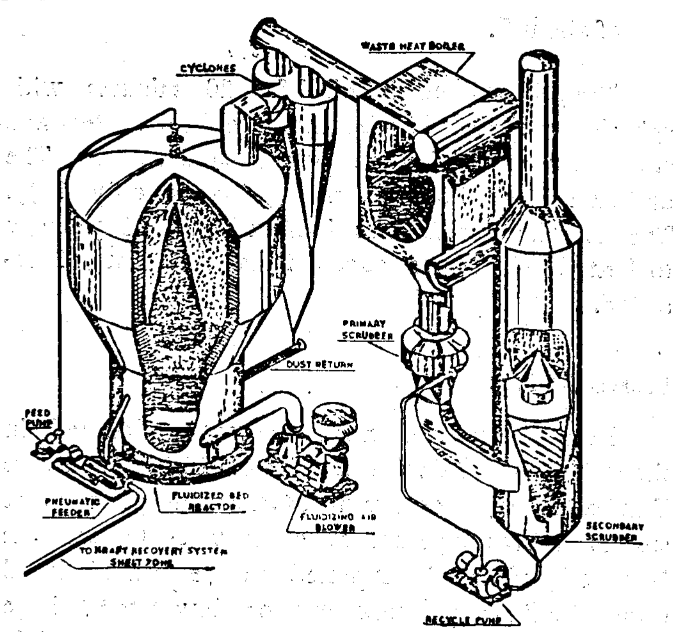

Fig. 4---FLUIDIZED BED COMBUSTION OF KRAFT LIQUOR

Constant bed temperature around 700°C is ensured. The black liquor organics burn liberating heat and inorganics deposit on growing into a spherical fluid bed pellets. Plellets (Na_2CO_3) can be transported pneumatically and lime causticized to get back NaOH. A major advantage of this process is that the unit is safe from explosion hazaards since no smelt is generated and that the waste heat boiler is physically separated from reactor.

Energy efficiency : Over all thermal efficiency for fluid bed system is as high as 64%, which is comparable with conventional system.

		Copeland system	Conventional system
1)	Steam energy recovery efficiency	28.5%	59.0%
2)	Low level energy recovery efficiency	35.9%	6.3%

Present Status :

Some of the units were installed and successfully operated. One such units was established in Syria in early 80's to process straw black liquor. Unfortunately there is no authentic is available on the performance. Some reports indicate that there was a tendency of the ash to melt due to fluctuations in reactor temperature.

One of the economic advantage of copeland fluid bed recovery system is that for additional load instead of going for additional Tomlinson furnace a fluid bed system would be much more economic.

2) Dry Pyrolysis Recovery :

The dry pyrolysis recovery involves four stages namely :

— dry solids evaporation
— pyrolysis
— Gasification, and
— Inorganic and heat recovery

In the first stage the black liquor from multiple effect evaporator, with concentration of 50-60% is further evaporated to almost dryness.

One commercially available dry solids evaporator uses oil as heat transfer medium and also to maintain pumpable slurry. The dry solids evaporation step accoplishes a major part of the objective to improve the energy efficiency of recovery.

Further as the volume of gases and vapour produced is small the equipment size will be smaller. Black liquor solids from the dry solids evaporator are subjected to pyrolysis with limited amount of gas containing oxygen from the gasifier.

The hot pyrolysed solids, containing residual carbon, are transfered to gasifier to complete the oxidation of organic matter. The gasifier is also operated with less air than required, for complete combustion of carbon.

The final key step is recovery of inorganic heat which is accomplished by employing suitable heat exchanger. The energy recovery efficiencies are given below :

	Dry pyrolysis	Conventional
— Energy recovery efficiency, %	55.6	43.3
— Low level energy recovery efficiency,%	21	21

Present Status :

The process concepts described clearly indicate several advantages of "Dry Pyrolysis" over conventional. There are possibilities of adapting or retrofitting in existing conveniional systems. However, great deal of effort and investments are required to prove commercial viability.

The molten smelt is tapped off as the combustible gases proceed onwards. This process is still at the research stage.

4. DARS/FERRITE PROCESS

DARS ie. Direct Alkali Regeneration System is one of the outstanding development in the area of chemical recovery technology. The process has attracted the attention of the whole world. The basic principle of the process involves combustion of concentrated black liquor and Fe_2O_3 or other amphoteric oxides to obtain a solid product ie. NaOH and Fe_2O_3 or other The reactions are given below. The flow sheet is illustrated in Figure.

Combustion :

$$\underset{(Na_2O)}{\text{Black liquor}} + Fe_2O_3 = Na_2Fe_2O_4$$

Leaching :

$$Na_2Fe_2O_4 + H_2O = 2NaOH + Fe_2O_3 + \text{Heat}$$

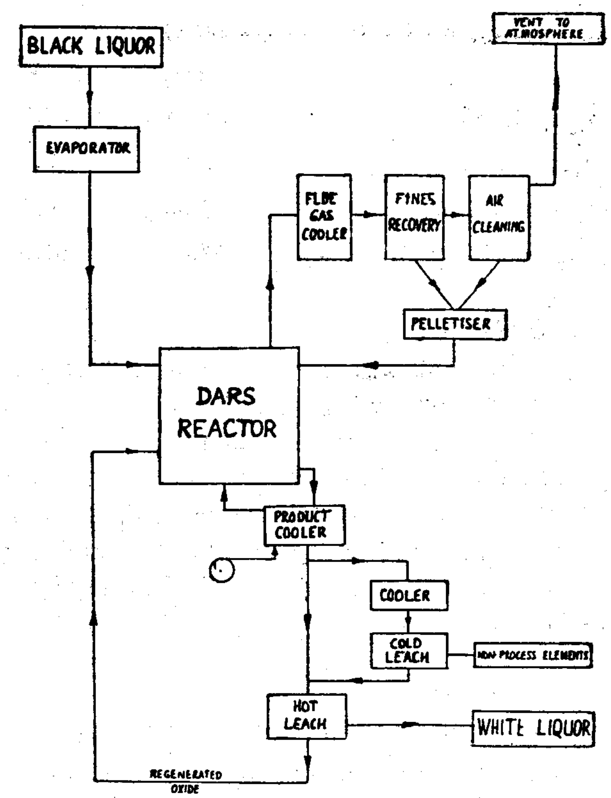

FIG.5- DARS FLOW DIAGRAM

Former reaction is endothermic while the later reaction is exothermic. Thus combustion and causticizations are effected in a single stage and single reaction vessel. The system eliminated lime causticization completely. The process is ideally suited for soda liquors. Some of the advantages of this process are :—

- Process is simple and flexible
- Does not require additional like causticization
- No smelt explosion hazards as the product is a solid mass
- The process is less capital intensive compared to conventional system.

Energy Requirements for DARS relative to kraft (1 tpd Basis)

	Kraft	DARS
Digester steam, GJ	3.47	3.40
Evaporator steam, GJ	4.36	3.35
Fuel for lime kiln, GJ	1.71	0.00
Relative change from conventional, GJ	0.0	—2.79

Relative Energy Efficiencies (1 tpd basis)

	Kraft	DARS
Heat input, GJ	23.15	23.08
Heat losses, GJ	7.55	8.93
Heat to steam, GJ	15.60	14.15
Thermal efficiency, %	67.4	61.3

Present Status

A 200 tpd unit was commissioned in Australia in 1986. A wheat straw based mill in Denmark has also commercialized the process and the plant is now operating on trial basis. Intensive research work on the application of this process to our small pulp mills based on non-wood fibers, is going on at CPPRI and hopefully a demonstration pilot plant will be ready by the end of 1990.

OPTIONS AND OPPORTUNITIES

With stringent legislation by pollution authorities and heavy recurring losses due to discharge of valuable chemic ls and biomass through spent pulping liquors, the option before small pulp and paper mills is to get themselves equipped with suitable system for treatment and recovery of cooking chemicals. Factors which determine the viability of any system are—productive capacity of the mill should meet minimum economic limit of the chosen system, technical feasibility and magnitude of pollution prevailing in the mill.

New technology always involves certain degree of risks. Although in the last two decades number of new processes developed have failed to live upto expectation when tried on commercial basis. Main reasons were-excessive complexity, unit operations with extreme requirements and incompatibility between stages. However DARS process has minimized above risks, as it is simple, flexible safe and unit operations are conventional. The process offers attractive opportunities to many mills, such as medium size mills and mills facing environmental problems and mills, who want to switch over to sulfur free pulping processes. Although extensive pilot plant studies have been carried out and two commercial scale units have come up, but the technology needs to be investigated for processing of spent pulping liquors from non-woody raw materials like bagasse & straws. The work on these lines are carried out actively at DARS pilot plants being installed at CPPRI. Neverthless there are indications that among the technologies developed, DARS process shows a promise of potential applications to small pulp mills and also as an alternative to conventional technology.

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