A new chemical recovery system based on indirect gasification of black liquor

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ABSTRACT

Conventional combustion routes require that the black liquor be concentrated to at least 45% solids in multiple effect evaporators and to about 60% solids in Direct Contact Evaporators, before firing into furnace. These pose serious problems in case of rice straw liquor, which tends to become highly viscous and to also precipitate out silica at concentrations above 35%. Further silica increases melting temperature of inorganics, thereby necessitating use of costly furnace oil, as supplementary fuel.

A new Chemical Recovery System (CRS), namely, MTCI's pulse enhanced indirect Gasification system, is being developed based on indirect gasification of black liquor, resulting in a solid residues in the *form of powder* that contains sodium carbonate and silica. By the adoption of pulse assisted combustion, the temperature of gasification is accomplished at temperatures lower than the melting point of inorganics. This critical *non-smelting feature* of the system together with the virtue of *indirect gasification* to accept feed stock at as low as 35% concentration, offers great potential for chemical recovery from all liquors without use of any auxiliary fuel. Also, the process results in the production of clean medium heating value gas.

For example, the overall chemical recovery efficiency is equal and the thermal efficiency is higher by 5 to 10% compared to conventional recovery boilers, when using bagasse black liquor at 45% solids as feed stock. The modular construction of these gasifiers render the CRS to be suitable for small mills of pulping capacities from 30 to 80 tonnes per day, and to be operated easily at turned down ratio of 50% and lower. Installation costs are cheaper or at least comparable to conventional recovery boilers

The results of pilot-scale test performed on jute black liquor from an Indian mill is reported in this Paper. Steady-state chemical recovery and gas production during the test are also discussed.

Introduction :

The classical method of recovering chemical from the black liquor generated from chemical pulping of bamboo and hard wood involves three important steps :

— Pre-evaporation of black liquor in multiple effect evaporator to at least about 45% solids.

— Combustion of black liquor (after further concentration to 60% solids) in a Chemical Recovery Boiler to form a smelt, which is dissolved in water to obtain green liquor.

— Recausticizing of green liquor (predominantly Na_2CO_3 solution) with lime to form white liquor (cooking liquor).

This method has been found to be generally accep-

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table to bamboo/wood/bagasse based liquors. However in the case of straw based liquors, the presence of high level of silica poses problems both in pre-evaporation and in combustion. When straw based spent liquor is concentrated, silica precipitation and increase in viscosity occur when concentration of black liquor is raised above 35%. Secondly since the combustion process leads to smelting of inorganics, the presence of silica requires higher temperature to be maintained in the furnace zone thereby necessitating use of expensive supplementary fuel, such as furnace oil.

Another constraint of the classical Chemical Recovery Boiler is that the combustion (furnace) and heat recovery (boiler) operations being in one single integral unit, scaling down of this system to smaller capacities (30-60 tpd of black liquor solids) and also co-generation of steam at this low capacity ranges are not economically feasible.

An alternate route of indirect gasification, which counters all these disadvantages is presented below, wherein all the inorganics in the black liquor are recovered in the dry form and all organics are converted to the gas phase to produce a clean medium heating value gas.

Review of Alternative Technologies :

An extensive summary of available/emerging technologies for identifying a viable chemical recovery system for small paper mills and also for rice straw based pulp mills was carried out by Esvin Tech about four years ago. This led to the conclusion that for silica rich liquor, gasification is a preferred route rather than combustion. The alternative routes are reviewed hereunder :

Molten Salt Gasification Process (1)

Champion International Corporation, USA, have carried out detailed pilot plant studies for the gasification of black liquor using their Molten Salt Gasification Process. In this process black liquor and air are fed continuously into a gasifier containing a molten salt pool maintained at about 900-1000 °C. While the organic matter is gasified by partial oxidation, inorganic compounds are melted and participate in the reaction. The products are a low Btu gas (120 Btu/scf) and a reduced melt analogous to that obtained in Tomlinson's recovery furnace. The process claims that black liquor gasification and use of the product gas in combined cycled co-generation system based on a gas turbines has high potential as an alternative to the conventional recovery boiler:

This process development has been so far only in pilot scale and has not been pursued further by Champion.

Chemrec High Temperature Gasification Process (2)

The Chemrec process developed by Chemrec AB Stockholm and being marketed by Kamyr AB Karlstad involves gasification of black liquor in the reactor at about 1000 °C by means of a plasma generator resulting in a combustible gas and salt smelt. The salt smelt is separated and recycled to the cooking process. Combustible gas is then cleaned and burnt in a conventional gas boiler to generate energy.

The process is supposed to be safer and more friendly to the environment by virtue of its reduced emission levels. However the capacity range for which this process can be applied is still much higher i.e. in the order of 30,000 to 50,000 tpa of pulping capacity. A full scale demonstration plant is proposed to be built.

ABB Direct Gasification Process (3)

ABB Combustion Engineering, Sweden, have carried out pilot plant trials on direct gasification of dry black liquor. The objective is to develop a technology that is expected to perform as well or better than a Tomlinson Chemical Recovery unit and reduce or eliminate the safety hazards that have come to be associated with recovery unit operations.

In this process, black liquor is sprayed on to bed fluidized with air at substoichrometric conditions). This results in the production of a low calorific gas (80-100 Btu/cu ft) diluted with products of combustion and inorganics in black liquor recovered as dry solids from the bed.

Though chemical recovery is comparable with conventional recovery furnace, the process development has so far been only on pilot plant scale and further tests are to be performed to ascertain the performance of the gasification process.

MTCI's low temperature Indirect Gasification Technology (4)

It may be observed that all the above process routes involve *direct gasification* of back liquor. The first two routes involve very high temperature leading to smelting of inorganics. While the third route involves low temperature gasification route only, it suffers from the disadvntage of all auto thermal gasifiers producing low Btu gas, due to dilution with products of combustion.

Whereas, M/s Manufacturing and Technology Conversion International (MTCI). Inc., USA have developed and demonstrated, at pilot scale the feasibility of *indirectly* gasifying black liquor by adopting pulse combustion techniques, whose potential advantages they have been investigating for various other feed stocks. They have designated this gasifier as "Thermo Chemical Conversion Reactor" (TCCR) System. The processing of this technology to commercialisation and the various advantages of the process are highlighted by Roger Grant (5.).

Uniqueness of the Proposed Process

The uniqueness of the proposed process lies in the full utilisation of the innovative features of the TCCR System to address even the special conditions required to recover chemical from rice straw liquor These are :

a) This indirect gasification technique permits low concentration of solids in the feed-an advantage for rice straw liquor, which poses silica precipitation problems, when concentrated above 35% in multiple effect evaporators.

b) Pulse assisted combustion adopted in the TCCR System has rendered gasification possible at temperatures below the melting point of inorganics (less than 650° C) - a factor so important for silica rich liquor since the silica combined with Na_2CO_3 can be recovered in powder form and hence expensive furnace oil need not be used to melt the inorganics coated with silica. The silica bound with inorganic salt discharged as powder. can be purged out of the system together with lime sludge during recausticizing operation.

c) The indirect gasification also produces synthesis gas of higher calorific value (2500 Kcal/cu.m) than the lower calorific value (1000 Kcal/cu.m) gas produced in direct gasification. This means the product gas can be recycled as source of heat to the pulse combustor and the surplus can be burnt in a conventional boilers with suitable burner arrangement.

d) The TCCR System can be built in modular capacities and has a high turn down ratio-both features are additional plus factors while addressing the needs of small paper mills and also big mills, planning for marginal capacity expansions but are limited in chemical recovery system.

Description of the Proposed Chemical Recoveery System

Based on the above unique features, a new Chemical Recovery System (CRS) has been evolved for treatment of silica rich black liquor derived from various sources. The Process Flow Sheet (Fig. 1) illustrates the typical process configuration of the CRS, the heart of which is the flow MTCI's TCCR System.

Salient features of TCCR System

The MTCI's gasifier comprises a steam fluidized bed containing an array of immersed heat transfer tubes (resonance tubes). Organic material that is introduced into the bed undergoes a rapid sequence of vaporization and pyrolysis reactions. Higher hydrocarbons released among the pyrolysis products are steam-cracked and partially reformed to produce low molecular weight species. Residual char retained within the bed is more slowly gasified by reaction with steam. The resulting product gas contain a high concentration of hydrogen (55-65% volume) and possess a higher heating value typically ranging from 2200 to 2700 Kcal/cu.m. The product gas after cleaning is refired in to the pulse combustor which supplies the requisite heat for the gasification process.

The physical principles involved in the operation of a pulse combustor are the same as those that govern

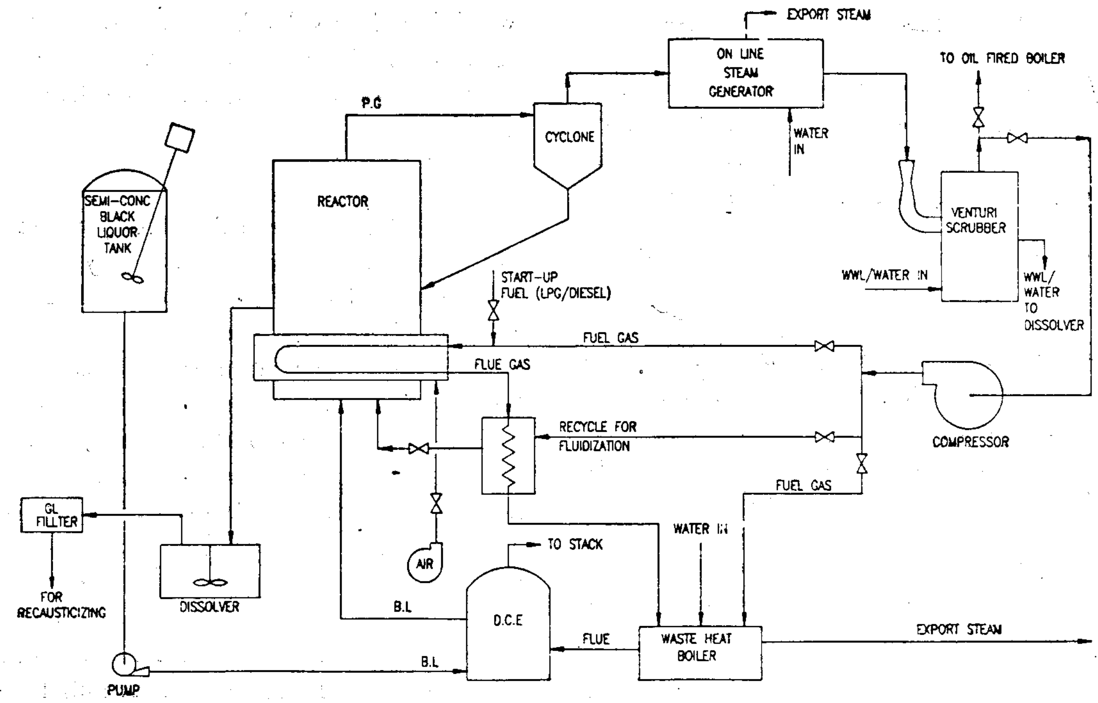

FIG. 1. SCHEMATIC OF INTEGRATED BLACK LIQUOR RECOVERY PLANT

the undesirable pulsations that sometimes plague conventional burners: however in the case of pulse burner combustion oscillations are intentionally induced by design in order to enhance combustion efficiency and heat transfer rate. Pulsations within the combustion chamber are translated to intense velocity fluctuations in the resonant fire tubes, which are immersed within the fluidized bed. These velocity fluctuations (plus or minus 180 m/s), which occur at design-controlled frequency (typically 30-300 Hz). intensely scrub the convective boundary layer formed on the inside surface of the fire tube, thereby enhancing heat transfer rates several-fold over non-pulsating systems. A critical feature of the pulsating combustion module results from its ability to provide delayed combustion within the resonant fire tube, thereby providing very uniform heat fluxes within the heat release zone of the gasifier. In this way maximum flame temperatures within the resonant fire tubes are substantially less than the adiabatic limit. This moderates the peak fire-tube wall temperature, allowing use of practical alloys of construction and preventing undesirable agglomeration of low-melting, ash constituents such as inorganic salts in black liquor.

Product Gas Cleaning and Recycling

The product gas exiting the gasifier get about650°C is fired and passed through a cyclone that removes entrained macro particles. The product gas is then further cooled in a heat recovery system (where steam can be raised) before further quenching and scrubbing in a venturi scrubber to get a clean and cool fuel gas. This fuel gas is partially refined into the pulse combustor as a heat source and the balance fuel gas is available as a net fuel gas export for firing into a conventional utility boiler of the mill. The sensible heat in the flue gas from combustor is recovered in a conventional waste heat boiler and direct contact evaporator.

Product Solids

The product salts discharged as dry solids from the bed goes to a dissolver tank as also the discharge from the Venturi scrubber. The residual carbon content in the product solids maintained around 2-3% to prevent possible agglomeration of bed material. This carbon is filtered out from the dissolver and recycled to the gasifier.

Pilot Scale Trials on Indian Black Liquor

To highlight the various advantages of the recovery system, to obtain information on steady-state operation and characteristics, a pilot scale test was performed on Indian Kraft black liquor derived from jute.

The schematic of the experimental black liquor gasification test rig used for the test is shown in Fig. 2.

Steam generated in boiler H-1 was utilized to fluidize the gasifier and heat the black liquor. The black liquor feed tank (V-1) is comprised of a steam-jacketed agitated vessel. Prior to entering the gasifier, the steam was superheated using the heat from the combustion flue gases. The steam was injected into the bed using a get of eight sparger tubes made from 1/4" SS tubing with 1/16" holes in them The bed fluidization velocity was maintained around 1.2 ft/sec.

The black liquor metering tank was positioned on a platform scale (to monitor feed rate) and the liquor was injected by a diaphragm metering pump (P-1) into the lower region of the gasifier using a single co-axial, steam-atomized injector. The black liquor was fed at 180°F.

The black liquor gasifier (R-1) represents the heart of the system. R-1 was an indirectly heated. fluidized bed steam gasifier. The heat for gasification was supplied by the in-bed surface formed from the resonance tubes of the pulse combustor. The resonance tubes were two U tubes (1.5" nominal bore pipe), which act as tail pipes of the pulse combustor. The gasifier lower shell was constructed from an 8" dia. stainless pipe and expands to a 12" dia free-board to allow improved disentrainment. The bed (typically calcium carbonate or sodium carbonate as inert) height was approximately five (5) feet. The pulsating combustor was fired using natural gas as fuel and a forced draft fan (F-1) was utilized to deliver combustion air to the combustor-air plenum.

V-1	BL TANK	X-2	VENTURI SCRUBBER	F-1	COMB. AIR BLOWER
H-1	STEAM BOILER	V-5	SCRUBBER TANK	P-1	B.L. PUMP
R-1	REACTOR	V-4	COLLECTION DRUM	P-2	FILTER PUMP
V-2	RECIRC. CYCLONE	V-6	FILTER TANKS	E-1	WATER COOLER
V-3	FINES CYCLONE	C-1	H2S SCRUBBER		

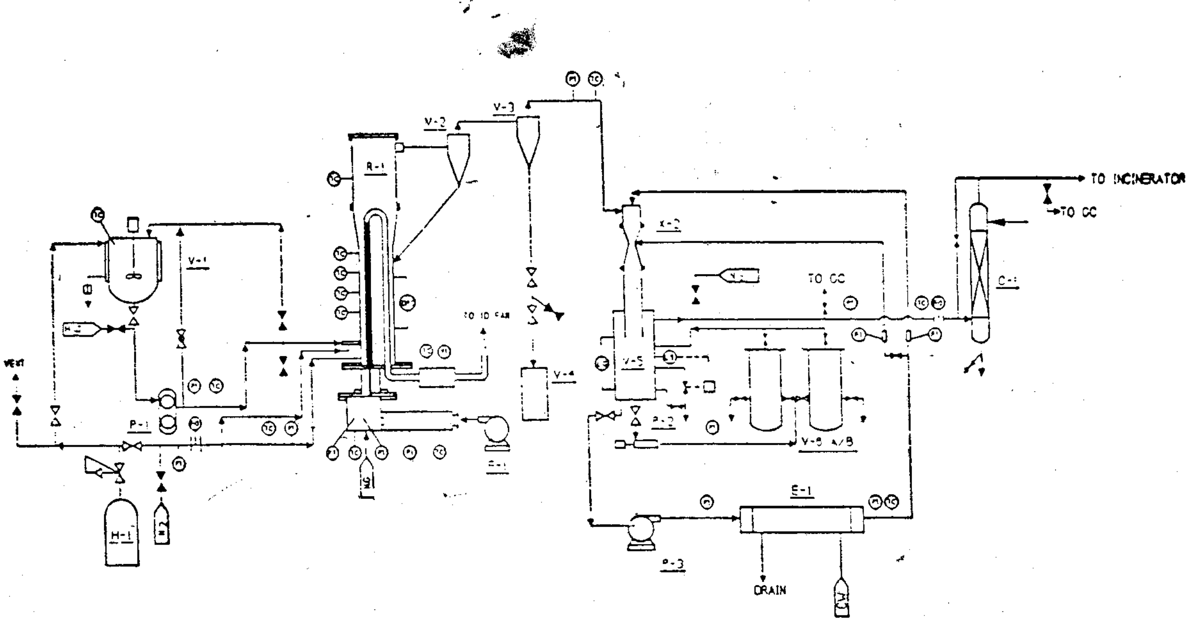

FIG. 2. PROCESS FLOW DIAGRAM FOR TEST RIG

Product gases from the fluid-bed reactor were directed to two cyclones in series. The first cyclone (V-2) functions in a complete recycle mode to return the coarse particles collected here to the bed. The product gases then enter a second fines cyclone (V-3) and the particles were collected in drum V-4.

The product gases then enter a venturi scrubber system, where the scrubber (X-2) provides high momentum contact between a circulating water stream and the product gas. This promotes the removal of fine particles, while simultaneously cooling the gas and condensing the steam contained in it. The recirculating scrubber water was cooled in the scrubber cooler (E-1) The scrubber water also passes through filter system (V-6 A/B) to remove accumulated solids in the tank.

The H_2S scrubbing system was made up of two static mixers (C-1) in series in the product gas line, where the gas was scrubbed against an alkaline solution (14.5%, % wt Na_2CO_3). The two static mixers had dimensions of 1/2" OD and 9" length.

After passing through the sulfur recovery column, the product gases were incinerated and vented through a polishing scrubber. The incinerator was supported by a continuous natural gas pilot flame.

Gas samples were withdrawn for analysis at two locations - one at the exit of the cyclone and the other at the exit of the H_2S scrubber. While the sample at the first point was used to estimate the H_2S content in the gas, the sample at the second point was used for the calculation of H_2S scrubbing efficiency.

The dry gas flow rate was determined by using an inert gas tracer technique. Incidentally. nitrogen was used to purge the pressure ports on the gasifier and its flow rate was carefully measured with a digital flow meter. By knowing the percentage nitrogen in the product gas stream from the gas chromatography analysis the flow rate of gas produced was determined.

The gasifier was operated at steady-state conditions at a bed temperature of 1050°F. This temperature is much below the melting point of sodium carbonate (1550°F). The black liquor feed was maintained around 20 lbs/hr for about six hours, at 50% concentration.

When black liquor is sprayed into the fluid bed, a significant fraction of the organic carbon rapidly pyrolyzes to gaseous species. A portion of the carbon form as a char layer deposited on the bed solids. This layer is gasified by reaction with steam. At steady-state, the bed carbon level remains essentially constant, since the char gasification rate equals the char deposition rate. All the inorganics in the black liquor would remain in the bed and recovered by taking it to a dissolving tank, the volume of the bed would increase unless the bed material was continuously withdrawn.

Periodical solid samples were withdrawn from the bed and the cyclone to analyse for accumulation of sodium carbonate in the bed and residual carbon.

The analysis of black liquor used for the test is presented in Table-1. The different operating conditions of the the test are listed in Table-1. A difference of less than 20 of between the maximum and minimum fluid bed temperature confirms excellent fluidization conditions maintained during the test.

The analysis of dry gas produced during the test is listed in Table-3. Analysis at the exit of the gasifier and at the scrubber are provided to highlight the quality of the gas produced from the gasifier and the efficiency of the H_2S scrubbers, the dry gas flow rate was calculated as 20 cu. ft per pound of feed black liquor solids.

Quality of gas produced by indirect gasification

A look at the gas composition provided in Table-3 shows that the gas produced has very high concentrations of hydrogen, typically ranging from 63-67% vol. The carbondioxide concentration of 20-25% Vol. and a carbon monoxide of 4 to 6 % Vol. reflects the effect of water gas shift reaction, which appears to be near equilibrium. The heating value of the gas produced was computed to be between 270-300 Btu/cu. ft.

The high levels of hydrogen concentration, the absence of any unnecessary diluent gas, and the range of the gas heating value, highlight the distinct advantage of the indirect gasification route. On the other hand, direct gasification (partial oxidation) process would result in a lower heating value of the gas along with presence of large quantities of diluents like nitrogen, in the gas produced.

TABLE—1
BLACK LIQUOR ANALYSIS
Consistency—50% solids
ELEMENTAL ANALYSIS

Element	weight %
Carbon	37.9
Hydrogen	4.3
Nitrogen	1.8
Sulfur	1.7
Oxygen	35.5
Sodium	19.4
Calorific value	3428 cal/gm [6170 Btu/lb]

TABLE—2
SUMMARY OF OPERATING CONDITIONS OF BLACK LIQUOR TEST

Bed Temperature		Combustor
Maximum (deg. F)	Minimum (deg. F)	Temperature (deg. F)
408	302	1815
924	881	1925
1060	1036	1292
1147	1129	1729
1064	1055	1284
1143	1124	1416
1030	1012	2018
1068	1052	2141
1056	1042	2090
1064	1048	2267
1091	1077	2279
1205	1190	2413

TABLE—3
PRODUCT GAS COMPOSITION

COMPONENT	BEFORE H_2S SCRUBBER (vol%)	AFTER H_2S SCRUBBER (vol%)
H_2	66.2—63.2	67.2—63.4
CH_4	7.2—5.2	7.3—5.2
CO	5.3—3.8	5.3—3.9
CO_2	24.1—22.6	25.4—22.5
H_2S	1.0—0.7	0.0—0.06
C_2H_6	0.73—0.43	0.73—0.42
C_2H_4	0.37—0.23	0.34—0.23
HHV OF GAS PRODUCED—273 to 305 Btu/cu. ft		

Chemical recovery from black liquor

While all the organics in the black liquor feed is gasified and leaves the gasifier, the inorganics in the feed would remain in the bed in the dry form without smelting, since the bed temperature is maintained below the smelting temperature of the inorganics.

The analysis of bed sample at the end of the test is presented in Table-4. The sodium recovery is calculated to be above 98%. Most of the sulfur present in the black liquor feed is converted into H_2S in the product gas. This makes it convenient to recover sulfur by scrubbing it with an alkaline solution. A sulfur recovery of 94% was achieved during the test.

TABLE—4
ANALYSIS OF PRODUCT SOLIDS FROM BED

Component	wt%
Moisture content	0.46
Sodium Carbonate	18.98
Carbon	5.40
Ash	0.48
Calcium Carbonate	74.68

Refiring of gas in Pulse Combustor

The gas at the exit of the H_2S scrubber was fired in a single tube self-aspirating pulse combustor. The pulse combustor lighted off without any difficulty and continued to burn efficiently even after the pilot flame was turned off. This trial indicates that the gas produced in the system can be conveniently refired in the pulse combustor to provide the energy required for gasification without having to depend on external fuel source.

Demonstration Plants to be set up in USA & India

The basic thrust in MTCI's development of TCCR, in the field of application of black liquor is from the point of view of twin advantages that the TCCR offers in American scene-firstly, elimination of the formation of smelt, which is corrosive and has caused boiler explosion in USA and secondly the modular construction of the TCCR System is found to be economically advantageous for American Paper mills desirous of marginal expansion (10% of 600 tpd pulp mills). Since most of the American mills have lime kiln and gas turbines (forming Part of the co-generation cycle) the product gas has a ready outlet, in one of these consumption points. Currently MTCI are building a demo plant of capacity 2.0 tph of black liquor solids for a Weyerhauser mill in North Carolina, slated for start-up in December 1992.

While so, Indian conditions are vastly different in that the spent liquor from the raw materials to be used cannot be concentrated to 67% solids since the spent liquor from agricultural residues become highly viscous at such concentrations. In addition to viscosity problem, the rice straw liquor, when concentrated beyond 35% solids, results in precipitation of silica. Yet another aspect is that small agro-based paper mills do not have either lime kilns or gas turbines and also cannot afford to use prohibitively expensive furnace oil or diesel oil as the source of fuel supply to the TCCR System. Hence the product gas has to be cleaned and reused in the system.

Accordingly, MTCI and ESVIN TECH propose to jointly develop a TCCR System suitable for small agro-based paper mills and the demonstration plant of capacity 500 kgs per hour of black liquor solids is being set up at the mill site of M/s Seshasayee Paper and Boards (SPB) Limited, Erode, Tamil Nadu. The commissioning of the same is slated for end-December 1992. This demo plant is being funded by The Industrial Credit and Investment Corporation of India Ltd (ICICI), and Industrial Development Bank of India(IDBI)under their Programme for Advancement of Commercial Technology (PACT) scheme and Venture Capital Fund (VCF) Scheme respectively to the extent of 80% of the total project cost.

Meanwhile MTCI have installed a similar size demo plant at a paper mill site in Ontario, California for gasification of waste sludge from this mill plant has been commissioned recently and has since gasified waste sludge in excess of 150,000 lbs and this experience will be utilized to optimize the working condition of the demo plant at Erode.

Conclusion

1. Conventional chemical recovery system involving combustion route may not be suitable for most of the agro-based raw materials, which give rise to black liquor containing high silica and of poor burning characteristics.
2. Gasification seems a better alternative for capturing volatile compounds and indirect gasification is still better to improve calorific value of gas produced.
3. The innovative strategy of using pulse combustion as a heat source for indirect gasification has further helped to carry out gasification at lower temperatures thus preventing melting of inorganics.
4. The results of the pilot scale testing clearly establish all the above mentioned advantages of the new recovery system. producing clean medium Btu gas from the organics in black liquor and very high efficiency of inorganics recovery. The overall thermal efficiency of this system at comparable operating conditions of a recovery boiler is expected to be about 10% higher.
5. MTCI's Indirect Gasification system by virtue of its ability to convert all sulfur in the liquor as H_2S to the gas phase, it has the versatility to handle kraft, sulfite or soda liquor.
6. MTCI's TCCR System has great potential not only for black liquor from agro-based pulp mills but also for various other feed stocks of similar charactertstics such as high inorganic content, low colorific value etc., including low grade coal and lignite.

Acknowledgement

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Literature cited

1&2 Alternative Kraft Recovery Process-H. Jeff empie, TAPPI, May 1991.

3 Development of a dry black liquor gasification process-Dr. E Dhalquist. R Jacobs-Proceedings of International Chemical Recovery Conference. Seattle, June 7-11, 1992.

4 Indirect Steam Gasification of Paper Mill Sludge Waste, TAPPI, October 1991.

5 Chemical Recovery-A Quiet Revolution - PPI, March 1992 (Page 40)