Chemical recovery boilers and recent developments

SATHYANATHAN V.T.*, XAVIER A. AND BASU S.S.*

I Introduction To Chemical Recovery Boilers

A simple schematic of the Kraft mill (Fig. 1) shows the basic flow cycles of which the chemical recovery furnace is a part. In the paper making process, wood chips are mechanically prepared from hard and soft woods and cooked to pulp in digesters under pressure with white liquor chemicals. The lignin are separated by hydrolysis to organic alcohols, acids, and some mercaptans. The cellulose pulp is then washed and prepared for the paper machine.

RECOVERY SYSTEM



A cooking liquor recovery cycle retrieves white liquor for the cook from the black liquor spent chemicals obtained from the pulp wash. Weak black liquor containing about 15 per cent $Na_2 CO_3$, $Na_2 SO_4$, $Na_2 S$ and the lignin organic is concentrated in multiple effect evaporators to about 50 per cent strong black liquor. Due to liquor characteristics, further concentration is often better done in a cascade evaporator where hot gaseous, stream contracts the liquor. Cycle

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make up chemicals, usually salt cake, are added to the resulting 68 per cent heavy liquor. At this concentration, the heating value is high enough to provide self sustaining oxidation with air to evaporate the remaining water, provide heat of reduction for chemical recovery and to provide additional heat liberation to warrant heat recovery in the steam generating sections of the recovery unit.

The Na₂ SO₄ is reduced endothermically with carbon to form Na₂ S which is smelted with the Na₂ CO₃ and dissolved to form green liquor The Na₂ CO₃ pith up slaked lime from the slaker and is then causticized to NaOH. CaCO₃ mud is filtered out leaving the cooking white liquor consisting of NaOH, Na₂ S and residual Na₂CO₃.

The BHEL spray type chemical recovery unit utilises a three-zone furnace principle. Fig 2 to perform the recovery function. The black liquor is introduced as a coarse spray through liquor nozzles located in the furnace walls. Moisture in the liquor is evaporated as the liquor drops through the furnace. The remaining solid material forms a spongy cone shaped pile on the furnace floor or hearth.

Primary air is introduced around the periphery of the furnace in order to pyrolyze the organic material in the dry solids. Oil or gas fired starting burners at the primary air level provide the heat required to start the reactions which then becomes self-sustaining under normal conditions The reactions described in the previous paragraph produce a molten ash which form a pool approximately 10 incpes deep on the furnace bottom. The bottom 4 inches of this ash are cooled by the furnace floor tubes and form a solid protective

^{*}Bharat Heavy Electricals Ltd Tiruchirapalli 620 014 (T.N. *



RECOVERY UNIT FURNACE ZONES

layer. The liquid ash is removed by decantation and flows into the main dissolving tank to form green liquor.

In order to provide a reducing atmosphere, only 65% of the total air required for combustion is supplied to the primary zone. As the organic material pyrolyzes and burns, it is swept upward and mixes with the tangentially introduced secondary air where combustion is completed. On many recovery boiler installations, provision is made to introduce auxiliary oil or gas at the secondary air level to augment the steam generation produced by the recovery process alone.

The nature of the process produces a high dust loading in the products of combustion. The furnace and heating surface arrangements are designed to cope with this high dust loading by incorporating the following features :

- 1 Tower type furnacs and sharply inclined nose arch
- 2 Wide spaced platen superheater
- 3 Vertical wide spaced tubes and low gas velocity in the boiler bank
- 4 Vertical ineline longitudinal fined economiser tubes
- 5 Liberal use of retractable soot blowers for cleaning all heating surfaces

The necessary degree of heat recovery is achieved by one of the following arrangements as determined by system requirements:

- 1. Economiser and direct gas contact cascade evaporator
- 2 Economiser and laminaire air heaters
- 3 Large Economiser
- 4 Laminaire air heaters
 - Ref. Figure 3.

As with our other standard designs, the V2R boilers incorporate welded wall construction, which is of special benefit at the base of the furnace where it prevents leakage of molten smelt and eliminates refractory maintenance.

Furnace safety supervisory controls are provided to minimize the potential for furnace explosions from the auxiliary fuel firing These controls are designed in accordance with the recommendations of the Black Liquor Recovery Boiler Advisory Committee U.S.A. The BLRBAC, U.S.A, recommendations also include provision for an emergency shutdown procedure including draining of the boiler in the event of a boiler or waterwall tube leak.



FIGURE-3

11 EFFECT OF OPERATING PARAMETER ON RECOVERY BOILER The effect of major operating variables of a recovery boiler is εs shown in Table below: MAJOR OPERATING VARIABLES OF A RECOVERY BOILER

Variable		Interim effect	Effect on boiler operation
1. 2. 3. 4. 5. 6.	Liquor flow Liquor concentration Liquor composition Liquor temp. Liquor pressure Liquor heating value	Coarseness of spray Char bed height Char bed distribution Liquor drying Rate of combustion Furnace turbulance	Combustion stability Carry over Smelt reduction Combustion stability Smelting rate Combustion stability carbon in green liquor
7. 8. 9. 10.	Liquor burning profile Total air flow Air temperature Primary/secondary	Furnace temp. Superheater fouling Combustion stability Exit gas temperature	Reduction efficiency Sulphur emission Steam generation Total sulphur emission
i 11.	air ratio Soot blowing	Fouling of heat transfer surface	Useful steam generated and exit gas temperature.

The maintenance of the recovery boiler due to the change on operating parameter is discussed below :

LIQUOR TEMPERATURE: This can lead to fine or very coarse spray which leads to plugging of gas path in banks, SH etc; or can result in poor combustion stability and loss of bed. In both the case, if unit has to be shut down, then it requires cleaning of the gas path. The actual effect of this parameter on liquor firing is given below :

The liquor temperature is the most important variable in regulating the droplet size of liquor spray. The liquor particles after flashing in the furnace should be about 10 to 15 mm diameter. This measures adequate drying and reduce the amount of burning char carried over to the superheaters. There is no particular temperature that is ideal for all bed conditions The correct value must be determined by each mill since chemical characteristics of the liquor like type of wood pulped, concentration of active alkali, type and percentage of make up chemicals, as well as physical factors like solids concentration, spray pressure, viscosity etc., influence the spray characteristics in addition to the temperature. A liquor temperature of 115°C will be a good value for starting liquor spray.

Once the liquor is burning properly, the liquor temperature may be changed in small steps of 1/2°C with a time interval of 45 minutes to 1 hour between every setting to allow furnace equilibrium to become re-established. Even a value of 105°C need not be considered too low, if it results in a stable bed and high reduction.

LIQUOR BURNING PROFILE

The liquor burning profile is an important variable to govern the reduction efficiency of furnace. This can be looked at as char bed depth and char bed burning temperature. The char bed depth can be indirectly correlated to the effect of oxygen concentration at the char bed interface The bed height can be adjusted easily by slight changes in black liquor temperature entering the furnace.

However, this method of control should be avoided, if at any time it forces the use of fine liquor spray. A better method is to regulate bed height by changing the ratio of primary to secondary air. By increasing this ratio heat release can be shifted downward towards the hearth thereby counteracting the bed cooling effect of lower liquor temperature necessary for a coarse spray. In order to obtain optimum reduction efficiency, a substantial height of char bed shall be maintained at all times as shown in Figure 4. The peak height of the bed should be about 1000 mm from the primary airport bottom.



FIGURE-4

The peripheral edge of the bed touching the furnace walls should be maintained at or within 300 mm below the bottom of primary air port. Char should always cover the stream of molten smelt flowing around the base to prevent oxidation of its sulphide content.

The bed temperature is mainly controlled by the amount of primary air, the dryness and size of liquor droplets reaching the bed surface. The basic control however, must be through liquor side and not by primary air.

It is very important to maintain a relatively high bed temperature and a reducing condition at the bed surface. These conditions favour the volatilisation of sodium. The reaction of volatile sodium with SO_2 to form Na_2SO_4 is an important function in the overall sulphur recovery. However, the d aw back to high sodium volatilisation rate is the increased amount of fume increasing the load to the dust collection systems.

High bed temperature also improves the cumbustion stability with less likelihood of black-outs. The emission of H_2S and SO_2 decrease with high bed temperatures. An optimum char burning condition shows up a 300 mm layer of bright, orange flame above the char bed. The optimum bed temperature is in the range of 1000 to 1100°C. A typical char bed temperature is shown in Figure 5



CHAR BED. FIGURE-5

Air Flow And Air Temperature

The total air flows rate is related to the liquor input and the liquor composition. The air flows should be adequate to give an excess air into the furnace, in the range of 15% to 20% so that incineration of odorous constituents like H2S and mercapants in the hot air-rich secondary air zone is possible. Variation of excess air to a recovery boiler has a very slight effect on the thermal efficiency. This can be seen from Figure-6. However, operation at very high excess air wood increase the carry over, draft loss in the gas side and hence the fan power consumption. Operation of a recovery unit with insufficient air flow is also possible in view of the fact that the hearth bed has to be a reducing atmosphere. Hower this would result in unburnt combustible and consequent reduction in thermal efficiency.

The distribution of air between primary and secondary zones contribute: very significantly to the reduction efficiency and iquor burning profile. Increasing primary air quantity will tend to increese char bed

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temperature, increase the burning rate and lower the reduction efficiency. It is equally important to distribute the primary air around the char bed. The effect of this ratio on liquor burning profile has been discussed earlier.

The air temperature is an important variable for controlling the temperature levels within the furnace. Normally recovery units are operated with an air temperature of 150°C. An increase in air temperature direct influences the combustion stability and steam flow. This has been illustrated in Figure 6. High air temperatures are required when burning liquors with a low heating value or during continued part load operation of the boiler or when solids concentration fired is low. On the other hand, low air temperatures can cause substantial emission af SO₂



Black Liquor Quality

The black liquor concentration entering the boiler the liquor firing concentration and the heating value are important qualities to be born in mind. The changes in these parameters can not only affect the recovery boiler operation but also the maintenance by increasing the fouling in heat transfer surfaces like SH, bank tubes etc. This can also lead to high corrosion rates at the precipitator sides.

Liquor concentration entering boiler is a variable tied up with the performance of multiple effect evaporators. The liquor solids concentration is normally supposed to be maintained at a selected value.

On the other side, the cascade evaporators with judicious selection of the auxiliaries will be able to accept a nominal variation in the inlet concentration (2 to 3%) by suitably adjusting the effective area of evaporator exposed to flue gas path. It shall be noted that only the inlet liquor concentration to the recovery unit is tied up with the steam generation irrespective of the firing concentration. Though the liquor combustion and bed stability greatly depends on the firing concentration.

The importance of high firing concentration has been emphasized earlier, under liquor burning profile. The optimum performance of a recovery unit is obtained at the highest possible concentration at the entry to the furnace.

The practical constraints in pumping very high viscosity liquor has limited the maximum concentration to about 72%. The normal value lies around 68% solids. The minimum firing concentration is limited to 58% solids, to comply with the BLRBAC requirement to prevent smelt water explosion.

A low firing concentration may also lead to fine spray and low bed conditions. Operating the recovery unit with a particle size less than 6 mm and a bed height less than 600 mm (from primary airport) has the following disadvantages :

- 1 Substantial increase in mechanical carry-over
- 2 Increased fouling of heat transfer surfaces
- 3 Accelerated fouling of primary airport

4 Low reduction efficiency

5 Poor combustion stability

6 Increased emission of H₂S and SO2

HIGHER HEATING VALUE OF BLACK LIQUOR is an important parameter in sizing a recovery furnace and significantly influences the combustion stability of the bed. The heating value of liquor is inversely proportional to the yield of pulp and depends on the raw materials Variation in liquor HHV effects on the thermal efficiency for the same operating conditions with changes only on the elemental analysis, corresponding to the variation in heating value. It may be noted that the thermal efficiency increases with increasing HHV.

As the HHV increase, the carbon and hydrogen content of the liquor increase with a corresponding decrease in the sodium and sulpour content. Hence, the losses due to dry flue gas and moisture due to hydrogen, slightly increase However, the heat of reaction correction and heat in smelt decreases. The net effect is an increase in efficiency.

OTHER PARAMETERS

Other parameters like soot blowing, make-up salt cake are also important as these also lead to fouling problem and subsequent maintenance in the boiler.

LOW BED FINE SPRAY OPERATION—A HIGH MAINTENANCE PRONE OPERATION

The suspension firing type recovery boilers when operated with fine spray low bed lead to lot of problems and cause a high maintenance of the boiler.

The reason why Fine Spray Low Bed (FSLB) is resorted to by many operator is the ease in operation and minimum attention to be given. They result in no rodding of the airports. It also gets rid of the black liquor easily and creates green liquor.

There are various problems which are caused due to FSLB operation those are :

- 1 Increased mechanical carry over of ash
- 2 Increased ash fouling of heat transfer surface
- 3 Increased primary air port fouling rate

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- 4 Decreased reduction efficiency
- 5 Increased smelt leak potential
- 6 Decreased burning stability

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7 Increased smelt water explosion Hazard

Due to such kind of operation, the recovery boiler gets plugged and results in high maintenance downtime.

IV. PROBLEMS FACED IN RECOVERY BOILERS

The major problems which are generally faced in a recovery boiler are :

- 1 Heat transfer surface fouling, SH, Bank tube, Eco
- 2 Cascade evaporator plugging
- 3 Precipitator ducts corrosion
- 4 High SH steam outlet temperature
- 5 Smelt water explosion
- 6 Waterwell corrosion in high pressure units.

These problems are basically caused due to improper operation, poor liquor quality and low flue gas temperature The details of each problems are not discussed in this paper. However, the fact remains all these problems lead to high maintenance requirement in recovery boilers.

Va OPTIMIZED THREE AIR DELIVERY SYSTEM FOR CHEMICAL RECOVERY BOILERS

AIR DELIVERY SYSTEM REQUIREMENT AND FUNCTION

An optimized air delivery system has a two fold function to perform. First is to create an atmosphere suitable for recovery of inorganics and second is to combust the organics to provide heat for generation of byproduct steam. To maximise the recovery of inorganics chemicals, the smelting areas of the furnace must be in an oxygen deficient 'Reducing' atmosphere so that inorganics recovered will be in useful form i e., Na₂S instead of Na₂SO₄. Alternatively to optimize the thermal efficiency of the unit, the organic materials must be exposed to oxygen rich 'Drying' atmosphere when the combustible can be burnt to completion and

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thereby liberate the required heat to produce steam. Further as the black liquor is introduced into the furnace with a moisture content of 30-40% before either process can begin, the Air-Delivery system has to evapo rate the moisture.

As a result of this multiple process demands, the chemical recovery boiler furnace can be divided into distinct zones, each fulfilling a different need. These are illustrated in fig. 7. The fuel is sprayed into the furnace at an elevation of 5-6 mtrs. Where it dries in flight before reaching the smelt bed. This first zone around the fuel entry is therefore referred to as the drying zone.



Once the fuel is dried, pyrolysis of the organic constituents will begin and this is the hot zone. Finally, the inorganic chemicals are reduced through an endo-

thermic reduction chemical reaction and recovered in smelt form. This occurs in the lowest part of the furnace and is called the bed-zone or hearth of the furnace.

The three processes occurring in the lower furnace; drying, pyrolysis and reduction are all temperature dependent. The high temperature is got from the partial combustion of the organics. The partially combusted material then rises up the furnace and then passes through the fourth and final zone because of the oxygen rich environment maintained there. Here the combustion process is complete.

EXISTING AIR SYSTEM

The existing air system as shown in fig. 7 has been supplied as part of BHEL's chemical recovery boiler so far. By admitting approximately 65% of total air flow through the primary air system (temperature raised in a common primary/secondary air heater) at low velocities, high bed temperatures and a reducing atmosphere is maintained.

This increases the reduction of the chemicals. At the same time by introducing the remaining 35% of hot air through the secondary air system at high velocities and turbulance, the oxidising atmosphere necessary to complete combustion are maintained. This increases the thermal efficiency of the boiler. In addition to this, low particle carryover and a reduced plugging potential were assured due to the relative air system/ liquor firing gun locations.

OPTIMISED AIR SYSTEM

For higher/middle capacity chemical recovery boiler the performance can be further improved with the new three tier air delivery system. As hearth area increases (larger furnace) to maintain sufficiently high temperature at the bed, higher than normal quantities of primary air will be required. This means an oxygen rich environment in the reduction zone which would decrease the chemical recovery potential of the boiler.

To create a good reduction zone near the bed and improve the performance of recovery boiler, the new

optimised air system has three air introduction into the boiler, i.e. primary, secondary and tertiary air. Hot primary air is introduced at the bed level, hot secondary air is admitted just above the bed and cold tertiary air is admitted in the upper furnace above the black liquor spray guns. (vide Fig. 7)

Primary air is introduced through ports angled downwards and with velocities not very excessive but sufficient to penetrate 1 to 2 meters towards the center of the bed. Primary air particle oxidises the carbon on the bed and generates heat to maintain the optimum bed temperature, shape and size. Secondary air is introduced 1 to 2 meters above the bed, horizontally at slightly higher velocities in to the furnace. Secondary air functions in supplying oxygen to burn some of the combustibles liberated from the bed in support of the requirement for higher temperature in The secondary air system penetrathe lower furnace tes the furnace cross-section to reach all the combustibles to promote chemical reaction activity, at the same time not increasing the oxygen concentration at bed surface, also disturbing the bed minimum.

Cold fertiary air provides the necessary turbulance to generate intimate mixing of air with the gases liberated from the lower furnace. Cold tertiary air gives a desirable cooling effect on the flue gases entering the upper furnace convection zones and also the density of cold air being greater, the momentum will aid in mixing. Tertiary air is admitted to the furnace at higher velocitics from furnace corners to form two conconcentric circles (ref. fig.8). It also shows the existing air delivery system.

In chemical recovery boilers, the first melting point of the ash is closer to 550-750 deg. C. All convective heat transfer sections (closely spaced) located in temperature zones above this value are susceptible to gas side plug-ging because of the "sticky" ash which adheres to the tubes. If there is significant gas temperature distribution unbalance accros the width of the boiler, as a result of the final air admission system, the boiler can be susceptible to preferential plugging on one side of the unit due to the higher temperature.

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Test results have indicated that a concentric tertiary air arrangement as adopted in the new design reduces the gas temperature imbalance accross the boiler width.

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This arrangement provides the optimum mixing needed to complete combustion and to reduce TRS emissions. Schematic layouts of three tier air system are shown in fig. 9.



AIR SYSTEM

FIG 9

V_b STATIONARY FIRING OF BLACK LIQUOR IN CHEMICAL RECOVERY BOILERS

The stationary firing concept optimizes overall boiler performance through improved zone control in the furnace. Good zone control results well defined drying, Pyrolysis and bed zones in the lower furnace, thus decreasing the gas temperature in the upper furnace. See fig. 10.



STATIONARY BLACK LIQUOR FIRING AND ZONE CONTROL IN LOWER FURNACE. FIG 10

Figure 11. shows the stationary firing of black liquor. Stationary firing is just not stopping the oscillation of the black liquor gun of the old design. Stationary black liquor firing without optimising the air system as described in the earlier section V_{a} will not always result in desired improvement.

The first priority in obtaining good furnace zoning is to obtain consistently coarse black liquor spray droplets evenly distributed accross an arrow vertical band covering the entire furnace cross-section. Operating experience and test results show that the flat spray nozzle held station ary provides best results.



A properly designed black liquor firing system with optimised air delivery system will result in :

- 1. Reduced gas temperature to upper furnace.
- 2. Reduced liquor particle carryover and reduced smelting in upper furnace.
- 3. Even gas distri bution in furnace.
- 4 Complete combustion with lower sulphur emissions and hence less sticky ash.
- 5. High reduction efficiency.

Ve INCREASED OPERATING CAPACITY THRO-UGH OPTIMISED AIR DELIVERY SYSTEM AND BLACK LIQUOR FIRING SYSTEM

The first problem that restricts overload operation in a chemical recovery boiler is plugging of the operating bank (first convection heat transfer section) Optimised air system and black liquor firing system reduce the plugging potential as detailed in previous sections. Optimising air system and modifying firing system offers an indirect, low downtime and less costly, means of augmenting operating capacity. By doing an extensive study on existing boiler, it will be possible to decide on the type and amount of modifications required to achieve desired overload.

Even though the maximum benefits of stationary firing can only be obtained by upgrading both black liquor and air systems, an evaluation will indic te what benefits could be obtained by a partial modification. For eg., on some boilers installing the right liquor nozzles, fixing the liquor guns at the proper angle and adjusting the existing air system operation may be sufficient to reduce carry over, plugging, improve bed controls, reduction etc., at overload. Some units with two level air system could be modified by introducing a three level air system. A solution will have to be worked out on a case by case basis. BHEL can perform a study on an existing unit which requires performance optimization or capacity upgradation and suggest modifications indicating benefits, down-time for modifications, cost involved etc.

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V_d OTHER DEVELOPMENTS

1. LOWER -FURNACE TUBE WASTAGE PRE-VENTION IN HIGH PRESSURE RECOVERY BOILERS

For chemical recovery boilers operating with steam pressure above 63 kg/cm^2 (g) additional lower furnace wall corrosion protection is required. Lower furnace protection may be necessary for high sulphidity smelts and for high chloride content black liquors.

Lower furnace water walls are protected by :

- (i) High chromium coatings by flame spray or plasma Spray-low initial cost but high degree of maintenance is involved.
- (ii) Chromising of lower-furnace is a process exclusive to M/S Combustion Engg., US., BHEL's collaborator. This process which is developed by M/S CE is a high temperature technique that metallurgically bonds chromium into the surface of the waterwall tubes.
- (iii) Composite tubes (vide fig. 12): This has been the most successful method of water wall production.
 High initial cost but minimum maintenance is involved.

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COMPOSITE TUBE FURNACE PANEL CONSTRUCTION

FIG. 12

2 SINGLE DRUM CHEMICAL RECOVERY BOILER

High pressure, high capacity recovery boilers are now being offerred with single drum design. This design enables to have widely spaced vertical heat transfer surfaces in place of closely spaced boiler bank tubes. The other features of single drum recovery boiler resembles more or less like that of conventional Bi-drum design like, three level air system, stationary black liquorgun etc.

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