Increased Recovery Boiler Capacity through Black Liqour Oxidation

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The production rate of a Kraft pulp mill is often limited by the capacity of the mills' recovery boiler. The recovery boiler burns black liquor, a byproduct of the Kraft process, in a water-walled furnace. The inorganic chemicals in the liquor are recovered as a smelt and the heat from the combustion of the organic material produces steam. The capacity of the boiler can be limited by Excessive fouling of the pendant heat transfer surfaces, The maximum acceptable steam production rate, TRS emissions, Excessive corrosion in the lower furnace due to high temperature and Particulate emissions in the flue gas. A mill has various options to alleviate these limitations, including, Air Flow optimization, Oxygen enrichment, High solids firing and Equipment upgrades. One further alternative is to oxidize the black liquor. Black liquor oxidation is an established technology originally used to control Total Reduced Sulfur (TRS) emissions from a direct contact evaporator. However, the process can also be used to relieve a number of boiler capacity limitations. The Riapsa Inc. Kraft mill in Americana Brazil operated an Air Products black liquor oxidation system to increase the capacity of their Low Odor recovery boilers. Previous to its installation, the boilers were at their maximum steaming rate and had a fouling problem. Additionally, the multiple effect evaporator set was at its liquor-processing limit. Results are presented which show a 30mt/d pulp production increase and a net steam savings of 165mt/day. The initial capital investment was returned within the first 4 months of operation.

INTRODUCTION

A recovery boiler is designed to 'recover' inorganic chemicals, burn the organic material in black liquor and convert the heat from the combustion process into steam. Black liquor at approximately 70% solids is sprayed in droplet form into a water-walled furnace. The droplet dries, pyrolyzes and the residual, which is primarily carbon and inorganic chemicals lands on a 'char' bed at the bottom of the furnace. The inorganic chemicals, primarily sodium carbonate and sodium sulfide, form a smelt that flows from the furnace into a smelt tank where the chemicals are dissolved in water. The char and pyrolysis products react with combustion air producing heat and flue gas. A portion of the heat is absorbed by radiation into the water walls of the furnace. The flue gases travel up the furnace; transfer heat to pendant heat transfer surfaces, (i.e., the super heater, boiler bank, and economizer), pass through an electrostatic precipitator and are finally discharge to atmosphere.

Boiler Limitations

Fouling

Some of the droplets fired into the furnace become entrained in the flue gas. If these droplets contact a pendant heat transfer surface while in a semi-molten state, they will stick, causing fouling. Soot blowers (high-pressure steam nozzles) are used to remove the deposit. However, if the rate of accumulation is excessive, the boiler becomes plugged and must be shut down and cleaned. The rate of fouling will be reduced if a means can be found to fire large droplets to the furnace, minimizing the flue gas velocity, and/or lowering the temperature of the gasses entering the pendant heat transfer surfaces.

Steaming Rate

Boilers are designed to produce steam by nucleate boiling. The term 'nucleate boiling' refers to the process where a steam bubble forms on the internal surface of a "steam" tube and then detaches. This produces high heat transfer and keeps the external tube surface at a reasonable temperature. If the tube absorbs too much energy the bubbles will merge, producing an annulus of steam at the internal tube surface. The rate of heat transfer to the water inside the tube drops dramatically and the tube surface temperature rises. This situation is called 'DNB', Departure from Nucleate Boiling, and must be avoided. The steaming rate at which there is risk of DNB can be predicted based upon the configuration of the boiler. This rate, with an appropriate safety factor, sets the upper limit on steaming rate.

TRS Emissions

The emission of TRS from a recovery boiler is typically regulated. Hydrogen sulfide, a TRS compound, is produced in the furnace and subsequently oxidized by combustion air. To avoid the emission of TRS, a mill must maintain an excess of oxygen in the flue gas. A limit on the firing rate of black liquor will occur when the ability of the force draft (FD) fan or the induced draft (ID) fan to maintain an adequate flue gas oxygen concentration is reached.

In a Direct Contact Evaporator (DCE) recovery boiler, TRS can also be produced in the DCE through the reaction:

$$NaSH + H_2O \rightarrow H_2S + NaOH$$

To achieve the regulated emission limits the NaSH in the black liquor is oxidized to $Na_2S_2O_3$. The firing rate of a DCE boiler can therefore be limited by the capacity of the oxidation system.

Particulate Emissions

The emission of particulate from a recovery boiler is regulated. In most cases, an Electrostatic Precipitator removes particulate in the flue gas to the regulated limit. The primary source of particulate matter is 'fume'. Fume is produced when sodium, which has been volatilized in the hot lower furnace, reacts with sulfur and carbon to produce submicron-sized particles of sodium sulfate and sodium carbonate. The amount of fume produced and hence the loading in the flue gas increases as the temperature in the lower furnace increases.

Black Liquor Oxidation (Blox)

Black liquor is a solution of water, wood constituents (e.g., lignin), sodium compounds (e.g., NaOH) and sulfur compounds (e.g., NaSH, commonly reported as Na_2S). In the black liquor oxidation process, the NaSH is converted to sodium thiosulfate via the reaction :

$$2NaSH + 2O_2 \rightarrow Na_2S_2O_3 + H_2O$$

Some of the oxygen fed to the system also reacts with the organic material in the liquor producing acids. Both reactions are exothermic, increase the oxygen content of the black liquor and lower the liquor heating value.

In the Air Products BLOX system, high purity oxygen is used as the oxidant. The process is designed to recover the heat of reaction which typically results in a 20% reduction in the live steam demand of the multiple effect evaporator set. The value of this recovered energy can be significant as documented in the commercial results section of this paper. The Air Products BLOX process has been in commercial use for over 20 years.

Impact of (BLOX) on Recovery Boiler Capacity

Fouling

Flue Gas Velocity

The oxidation process increases the oxygen content of the black liquor (e.g., Na_2S is converted to $Na_2S_2O_3$). This oxygen is released in the furnace and becomes immediately available for combustion. For every cubic metre of oxygen used in the oxidation process, the combustion air and flue gas volume is reduced by 3.78 m^3. This reduces the flue gas velocity and thus the rate of particle carryover into the upper heat transfer surfaces.

Upper Furnace Temperature

When the products of the oxidation reaction decompose in the furnace, and endotherm is produced (e.g., $Na_2S_2O_3$ decomposes to Na_2S). This endotherm absorbs heat from the combustion reaction lowering the total energy release in the lower furnace. If the heat transfer to the water walls of the furnace is held constant, the temperature of the flue gas exiting the furnace (i.e., entering the pendent heat transfer surface) will be lower for a constant firing rate. This will also lower the temperature of the carryover particles. The result is a higher percentage of particles in the solid vs. semi-molten state. Therefore fewer particles "stick" to the pendant heat transfer surfaces. When the firing rate is increase the total energy release will increase to the base case level as well as the percent of particles in the semi-molten state.

It should be noted that the temperature in the lower furnace is not necessarily lower when firing oxidized black liquor. The temperature in this section of the furnace is a function of the amount of oxygen reacted, and the endotherm associated with drying, pyrolysis and decomposition of the oxidation products. With oxidized black liquor, the temperature in the lower furnace will remain constant if the amount of oxygen reacting is increased such that it offsets the endotherm associated with the decomposition of the reaction products of the BLOX process. This situation will occur if the combustion air to the lower furnace is held constant.

Liquor Droplet Size

One of the parameters that influence the size of the black liquor droplet, which may be fired to the boiler, is the rate of combustion. When firing oxidized black liquor the oxidation products (e.g., $Na_2S_2O_3$) decompose and the oxygen is released at the same time that the pyrolysis gases are produced. The oxygen contacts the pyrolysis gases in the boundary layer around the particle, enhancing the combustion rate. As a result, the amount of carbon reaching the char bed is reduced. The amount of carbon reaching the bed can be returned to the base case level by increasing the droplet size. The larger droplets have more downward momentum and are less likely to be carried up the furnace.

Steam Limitation

The best way to demonstrate the value of BLOX for a steam limited boiler is by way of example. Assume the recovery boiler steaming limit is 250,000 Kg/hr, the enthalpy of the steam is 2,200 Kj/Kg, the black liquor heating value is 13,540 Kj/(Kg black liquor solids), and the boiler efficiency is 65%. The maximum liquor firing rate is then :

Firing Rate = (250,000 Kg/hr × 2,200 Kj/Kg/ 65%/ 13,540 Kj/Kg)×24

= 1.50 mm Kg BLS/day.

At a Na_2S concentration of 35g/l (at 50% solids), approximately 60 mt/d of oxygen can be reacted with the black liquor. This will reduce the steaming rate by approximately 17,500 Kg/hr. Therefore, the new maximum firing rate will be :

Firing Rate = 1.50 mm Kg BLS/day ×

(250,000)(250,000-17,500)

= 1.61 mm Kg BLS/day (8%)

In this example, the use of black liquor oxidation would increase the capacity of a steam limited boiler by approximately 8%.

TRS Emissions

TRS emissions are strongly associated with the amount of excess oxygen in the furnace flue gas. As discussed previously, BLOX enriched the furnace with oxygen. Therefore, more liquor can be fired for a fixed flue gas/combustion air flow rate and a constant flue gas oxygen concentration.

Particulate Emissions

The temperature and thus the fuming rate in the lower furnace is a function of the heat flux (Kj/m^3). The heat flux in the lower furnace is maintained when the firing rate of oxidized black liquor is increased. Therefore, the fuming rate at the higher liquor firing rate will be approximately equal to the base case. Further, the performance of an ESP is strongly dependent on the gas velocity through the unit. When oxidized liquor is fired to the boiler, the specific flue gas volume (m^3/Kg BLS) is lower. Therefore the gas velocity through the ESP can be maintained at a higher firing rate.

Commercial Results

The Ripasa mill in Americana Brazil produces fine paper. A bleached Kraft pulp mill located on site provides pulp for the paper machines. In the late 1990's, the recovery area limited Kraft pulp production and the mill had to purchase additional market pulp to meet the needs of the paper machines. The boilers were operating at their steaming limit, they required cleaning once a month, the ID fan capacity became the limitation in the month previous to the annual shutdown, and the evaporator surface condensor was operating at its limit.

In 1999, Ripasa installed an Air Products black liquor oxidation system. The system was designed to handle 90 m^3/hr of black liquor at a solids concentration of 45% and a Na_2S concentration of 32g/l. The design oxygen flow was 45mt/d. The process was installed between strong black liquor storage and the concentrator. The energy from the oxidation reaction was recovered in a condensor where demineralized boiler feedwater was heated. Full operation began in January 2000. After startup, it was found that an analytical error had been made and the actual Na_2S concentration was 18g/l.

Results from the first 9 months of operation were compared to a base 9 months period in 1999. It was agreed that normalized the results to pulp production was the best method of determining the overall benefits of the process.

Pulp Production

The average pulp production increase was 3.4%. The safe steaming rate was the ultimate limitation.

Production Rate mt/d

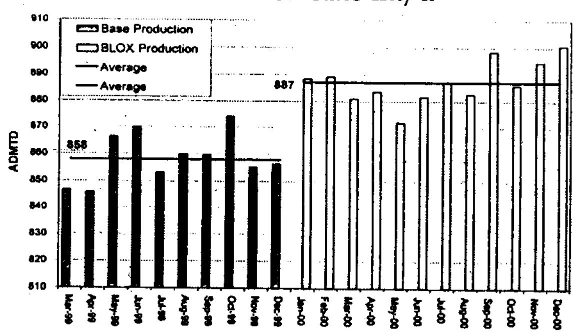

Fig. 1: Increase in Pulp Production

The rate of fouling of the boiler was not aggravated at the higher firing rates and the evaporation capacity provide by the BLOX systems was greater than the amount needed for the higher production rate (i.e., the condensor loading remained constant).

Figure 2 doucuments the tonnes of production increase per tonne of oxygen consumed. The predicted pulp/oxygen raito was 1.0 mtpulp/mt oxygen. The actual was 1.25.

Tonnes of Pulp per Tonne of Oxygen

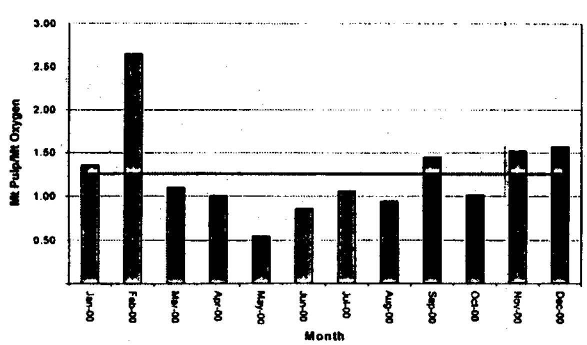

Fig. 2: Additional Tonnes of Pulp per Tonne of Oxygen

Energy Balance

The BLOX system was configured to maximize energy recovery. Liquor entered the system at 43% solids and exited at 48% solids. This dramatically lowered the steam demand of the concentrator and provided energy to heat boiler feedwater. The vapour from the concentrator dome is sent to a condensor, and the majority of the water from the condensor is sent to a cooling tower. Therefore, the savings in concentrator and deaerator steam represented a net energy savings to the mill. The steam demand of the evaporator set was expected to remain constant, however, the outlet solids concentration was expected to drop slight due to the higher flow rate.

The following graphs are normalized to pulp production. For example, the base case steam flow to the multiple effects evaporator set was 34.5mt/hour and the flow in the BLOX case was 35.4 mt/hour, for a gross increase of 0.9 mt/hour. However, the base case production was 858 mt/d, which

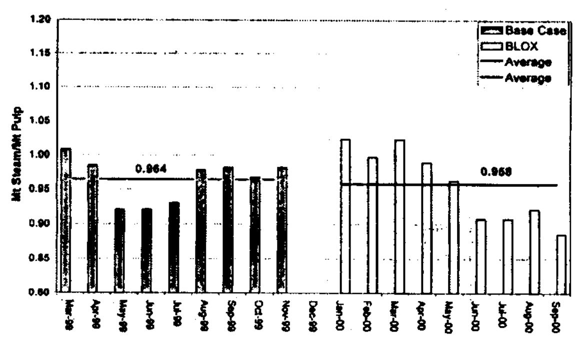

Fig. 3: Evaporator Steam Demand

translated into a steam/pulp ratio of 0.964 (mt steam/mt pulp) while the BLOX case was 0.958. The specific steam demand of the evaporator set

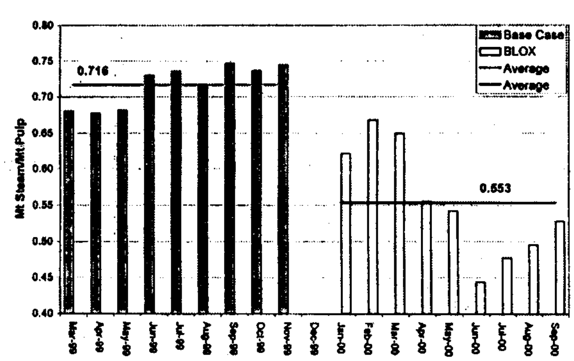

Fig. 4: Concentrator Steam Demand

decreased by <1.0% which was as predicted. However, once the operators adjusted to the system changes the savings increased to 7% in the last 4 months.

The steam saving in the concentrator followed the prediction fairly well. The lower savings in January through March are related to operator adjustments. During these months, the liquor solids concentration from the concentrator was higher then normal. The average reduction in concentrator steam demand was 23%.

The steam required to heat demineralized water was reduced by 28%. This was less than predicted due to fluctuations in the flow of boiler feedwater to the BLOX condensor.

Boiler Feedwater Steam Demand

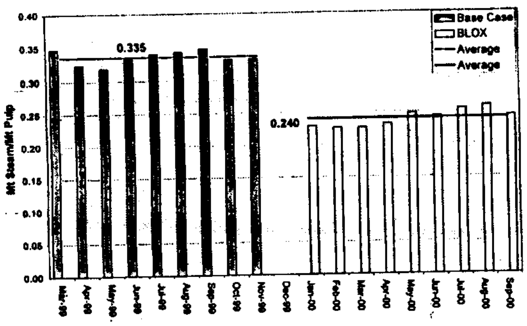

Fig. 5: Demineralized Water Heating

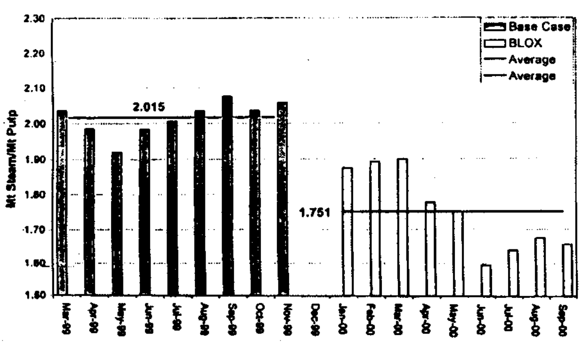

Fig. 6: Total Evaporator System Steam Demand

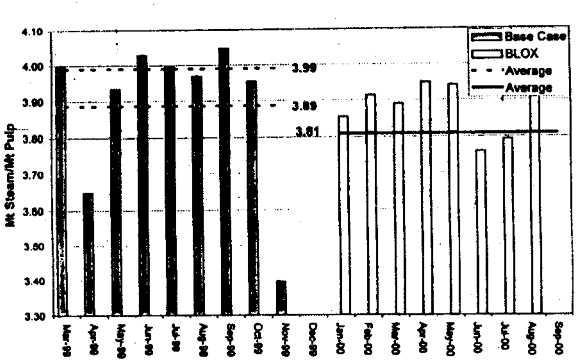

Fig. 7: Recovery Boiler Steam Production

The total steam demand of the evaporator/ demineralized water system was reduced by 13%, which was right in line with the predicted value.

The specific steam production from the boiler was reduced by between 2.1 and 4.6%. The lower base case average of 3.89 mt steam/mt pulp includes April and November, which on a statistical basis would be considered outliers. The average when these months are excluded was 3.99. There is a reasonable correlation between the reduction in specific steam production and the percent pulp production increase.

The net specific steam production from the recovery area increased by 10%, which was higher than the predicted value. In absolute terms, this difference represented a net savings of approximately 164mt/ day of steam. At a typical energy cost of $ 12/mt of steam, the yearly savings would be almost $700.000.

Net Steam to Mill

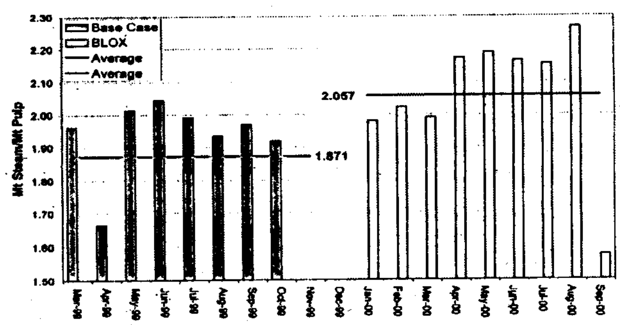

Fig. 7: Overall Steam Production

CONCLUSION

The Air Product BLOX system dramatically reduced the operating cost of the Ripasa fine paper mill in Americana Brazil. The process is very stable and requires little operator attention. A comparison between mill operation in the year previous to the installation of the BLOX system and after 9 months of operation demonstrated :

- A 30 mt/d increase in pulp production with an average oxygen consumption of 24mt/d
- A 164mt/d steam production increase from the recovery area to the mill.
- That the capital investment for an Air Products BLOX system can be returned within 4 months of startup.