NEW TECHNOLOGY FOR EMISSION CONTROL IN MODERN KRAFT RECOVERY BOILERS

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Abstract

The recovery boiler in an old pulp mill is often a large source of SO$_2$, TRS, NO$_x$ and CO emissions to the environment.

The emissions from modern kraft recovery boilers are much lower than from 20–30 year old units. It is the state of the art to rebuild old units to eliminate SO$_2$, TRS and CO emissions and at the same time increase the capacity of the unit. In the last couple of years, techniques have also been demonstrated that minimize the NO$_x$ emissions.

Introduction

The recovery boiler is one of the most important production units of the kraft pulp mill. Being both a chemical reactor for recovering of chemicals from the pulping process as well as an energy recovery process for steam and power production, the recovery boiler constitutes the heart of the kraft pulp mill.

The first Tomlinson recovery boiler in Europe was delivered by Götaverken to the Husum kraft pulp mill in 1936. For more than fifty years the Tomlinson type recovery boiler has been continuously developed to meet increasing demands for capacity, thermal efficiency, safety, availability as well as emission control.

The demands for emission control were for many years not very high and recovery boilers emitted large amounts of particles, SO$_2$ and TRS (total reduced sulfur compounds). Recovery boilers equipped with direct contact evaporators emitted for example well above 100 ppm TRS to the atmosphere.

During the last decades, great improvements have, however, been made regarding control of emissions from the recovery boilers as well as the rest of the pulp mill.

The emission of sulfur in Sweden is illustrated in Table 1 for the years 1980 and 1988. The total sulfur emission in Sweden has been reduced by about 60% during 1980's. During the same time, the Pulp & Paper Industry reduced its emission of sulfur by more than 70%. The specific emission in 1988 was 1.7 kg S/t pulp.

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TABLE 1. Emissions of sulfur in Sweden

<table>
<thead>
<tr>
<th>Year</th>
<th>1980</th>
<th>1988</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>t S/year</td>
<td>257 000</td>
</tr>
<tr>
<td>Pulp &amp; Paper</td>
<td>t S/year</td>
<td>48 000*</td>
</tr>
<tr>
<td>Kraft Pulp Mills</td>
<td>t S/year</td>
<td>32 800*</td>
</tr>
<tr>
<td>Kraft Pulp Mills</td>
<td>kg S/t pulp</td>
<td>6.1</td>
</tr>
</tbody>
</table>

* 50 – 55 % from oil firing

Less than 15% of the total emission of sulfur in Sweden now comes from the Pulp & Paper Industry, the dominating source being the energy generation sector. The emission of sulfur originating both from domestic sources and from surrounding countries is, however, still too high to avoid acidification. Although the Pulp & Paper Industry only contributes with a minor part of the emission of sulfur, a single pulp mill still constitutes a large single source for sulfur emission. Further reduction in permitted sulfur emission has been announced by the Swedish authorities both for energy generation and for pulp & paper production.

During the last decade an increasing knowledge with respect to the negative environmental effect of nitrogen oxides ($NO_x = NO + NO_2$) through acidification, overfertilization and ozone formation has resulted in more stringent demands for limitation of $NO_x$ emission from all combustion processes.

The concentration of $NO_x$ in the flue gases from recovery boilers is in the range of 4070 mg/MJ (based on net heating value of the fuel in reducing atmosphere) which, however, is low in comparison with other combustion processes. Despite this relatively low flue gas $NO_x$ concentration, kraft recovery boilers still are great $NO_x$ emission sources because of their totally large flue gas volumes.

Typical average values for the concentration of the most important pollutants in the recovery boiler flue gas in a Swedish kraft pulp mill are shown in Table 2.

TABLE 2. Typical emissions from Swedish kraft recovery boilers

<table>
<thead>
<tr>
<th>Particulates</th>
<th>(\text{mg/m}^3\text{n})</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRS</td>
<td>ppmv</td>
<td>0 – 5</td>
</tr>
<tr>
<td>(SO_2)</td>
<td>ppmv</td>
<td>50 – 300</td>
</tr>
<tr>
<td>(NO_x)</td>
<td>ppmv</td>
<td>60 – 100*</td>
</tr>
<tr>
<td>CO</td>
<td>ppmv</td>
<td>300</td>
</tr>
</tbody>
</table>

Dry gas at 3% \(O_2\)

* 40 – 70 mg NO\(_x\)/m\(^3\)n
In Table 3 are shown both guaranteed and performance test data from a recently started up North-American Göta Verken recovery boiler. These values represent the most stringent emission limits of all delivered Göta Verken recovery boilers to date.

**TABLE 3. Emissions from a modern North-American Göta Verken kraft recovery boiler**

<table>
<thead>
<tr>
<th></th>
<th>Guarantees</th>
<th>Performance test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulates</td>
<td>mg/m³n</td>
<td>70</td>
</tr>
<tr>
<td>TRS</td>
<td>ppmv</td>
<td>7</td>
</tr>
<tr>
<td>SO₂</td>
<td>ppmv</td>
<td>210</td>
</tr>
<tr>
<td>NOₓ</td>
<td>ppmv</td>
<td>110</td>
</tr>
<tr>
<td>CO</td>
<td>ppmv</td>
<td>300</td>
</tr>
<tr>
<td>VOC</td>
<td>mg/m³n</td>
<td>65</td>
</tr>
<tr>
<td>Dry gas at 3% O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC = Volatile Organic Compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>* S/Na₂ = 28 - 30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Below is discussed the status of recovery boiler emission control with respect to internal measures for reduction of TRS, SO₂ and CO as well as new developments for reductions of NOₓ.

**Status of Recovery Boiler Emission Control**

The fundamental mechanism for the formation and control of SO₂ and TRS in recovery boilers have been known for many years and with a gradual introduction of modern combustion air system, computer control systems, automatic air port cleaning equipment as well as high black liquor dry solids evaporators it has been possible to obtain the low emission levels given in Tables 2 and 3.

In Figure 1 is illustrated the primary emission of sodium and sulfur as well as the resulting SO₂ emission versus the furnace temperature based on a thermodynamic calculation presented by Borg et al (1). According to the model, SO₂ will be formed if more sulfur is emitted from the combustion zone than the corresponding emission of sodium for sulfur capturing as Na₂SO₄. The figure shows a very high influence of the furnace temperature on the SO₂ emission.
For optimum control of combustion conditions in the recovery boiler, Götaverken in 1960 introduced the separately fed three level air system. With the strong relationship between SO₂ and combustion temperature, the proper adjustment of combustion air to the different air levels is very important.

Equally important for a proper combustion and low SO₂ emission is the proper distribution of air around the boiler on all air levels. For this reason, Götaverken in 1973 introduced the RODDINGMASTER System for automatic cleaning of primary air ports from frozen smelt at present frequent intervals. If the frozen smelt is not constantly removed, air flow will vary causing upsets in reduction efficiency and emissions. With RODDINGMASTER the combustion process will stabilize which makes computer control possible.

Today, the RODDINGMASTER system has also been installed in the secondary air register in some recovery boilers for minimum air flow variation in the combustion zone.

In 1981, the Mönsterås Pulp Mill in Sweden initiated a joint development project together with ASEA, Götaverken Energy and STFI for better recovery boiler control. The primary goal for the project was better SO₂ emission control an increased availability and liquor throughput. The project involved fundamental laboratory studies, development of new control methods and new equipment for measurement and control.

Mönsterås Mill began operating with the new Advanced Control system (BLRBOMASTER) in May 1984. Already during its first year of operation, Mönsterås experienced considerable savings in operational costs, reduced excess air by more than 50%, reduced SO₂ emission to 2.3 kg SO₂/t pulp and practical elimination of TRS.

The BLRBOMASTER System consists of nine control modules which are illustrated in Figure 2.

The burning intensity module applies the fundamental relationship illustrated in Figure 1 between burning intensity (furnace temperature) and sodium/sulfur emission from the furnace. Changes in the sodium/sulfur emission from the furnace can be determined from the dust content as well as SO₂ content of the flue gas and the Ph value of the flue gas dust. This data is utilized in computing the burning intensity coefficient of the boiler.

The purpose of the control is to stabilize the burning intensity, which involves a qualified trend analysis because of the marked nonlinearity between for example SO₂ and the quantities of primary and secondary air respectively as illustrated in Figure 3 as presented by Herngren (2).
Final combustion control is achieved by measurement of the flue gas content of CO, which is used as an indicator of uncombusted substances, and O₂ followed by control the tertiary air flow and pressure to the boiler. This control provides stable operation of excess air at varying production rates while retaining a suitable CO content in the flue gas.

During the 80's the black liquor dry solids in new evaporation plants have increased from 68% up to 75% DS. The dry solids standard of the 70's was 65% and many pulp mills operate their evaporation plant (from the 70's) at this level.

With an increased black liquor dry solids to our most recent recovery boiler installations, the combustion has stabilized and the burning intensity has increased. As a result of this increase in burning intensity, the emission of SO₂ has practically been reduced to zero.

The added effect of the following discussed measures enables very low emission of both SO₂ and TRS as well as CO over a wide load range and up to high sulfidity levels.

Modern three level air system
RODDINGMASTER for automatic air port cleaning
BLRBOMASTER for computer control
High dry solids evaporation

The normal operation range for SO₂ emission versus S/Na₂ in the black liquor is illustrated in Figure 4 for a black liquor dry solids content of 65–67%. The lower level of the operation range represents the SO₂ flue gas concentration with modern three level air system, RODDINGMASTER and BLRBOMASTER in operation. With increased dry solids, the curve will move to higher S/Na₂ values. It is obvious from the figure that a proper control of SO₂ emissions to low levels requires good control of the sulfur balance for the whole mill.

With the BLRBOMASTER system in operation in the referred North–American recovery boiler in Table 3 the best balance for both reduction efficiency, combustion stability, and NOₓ emission was achieved when SO₂ was balanced at 30–50 ppm.

Pulp mills with high intakes of chlorides to a too high burning intensity in the recovery furnace might make chlorides accumulate in an internal recovery boiler recycle stream of NaCl with a subsequent risk of increased fouling of the heating surfaces.

**Development of NOₓ Reduction Techniques**

With the development of new techniques for recovery boiler control the trend for particulates, SO₂, TRS and CO emissions have been decreasing.

The formation mechanisms for the emission components SO₂, NOₓ, CO, and TRS are interrelated in the recovery furnace.
The interrelationship between CO and TRS is fairly easy to understand since both components can be seen as a result of incomplete combustion. There is an interrelation between NOx and CO as well as between NOx and SO2 which makes it difficult to achieve low emission figures for all three pollutants at the same time.

This interrelation has also caused a trend of slightly increasing NOx emissions in modern high efficiency boilers. Some of the reasons for this trend are:

- Increased black liquor dry solids
- Increased furnace loads
- High degree of SO2 reduction
- Demands for lower CO/TRS emission

The strongest interrelation is between NOx and CO since the formation of NOx and combustion of CO both depend upon the concentration of O2 in the combustion zone. For the North–American boiler referred to in Table 3, this interrelation necessitated a special tuning of the BLRBOMASTER System delivered with the recovery boiler to be able to meet both NOx and CO guarantees simultaneously.

To be able to meet the expected more stringent demands both for NOx and CO emissions from recovery boilers, Götaverken Energy has investigated both selective non-catalytic reduction (SNCR) as well as combustion control measures. A comparison of relative costs and efficiencies of both combustion control and SNCR as well as selective catalytic reduction (SCR) presented by Epperly et al (3) is shown in Figure 5.

The SNCR test was initiated by Södra Skogsägarna who commissioned a full scale demonstration of the NOxOUT(R) Process in the existing Götaverken recovery boiler at Mönsterås in co-operation with Petrokraft.

In the NOxOUT process NO is reduced by urea to nitrogen, carbon dioxide and water according to the reaction:

\[
2\text{NO} + (\text{NH}_2)\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}
\]

The reaction normally occurs within a narrow temperature range around 1000°C. If the temperature is too high, more NOx is produced and if the temperature window for reduction is widened and the by–production of ammonia is suppressed by chemical enhancers.

Figure 6 shows the NOx emission at the beginning of the final two weeks continuous verification operation in June–July 1990.

The by–product of NH3 was only 5 mg/m³n dry gas with the NOxOUT process in operation.
The result of the demonstration showed that more than 60% reduction was achieved despite a low initial NO\textsubscript{x} level. No disturbances or other negative effects on the operation of the recovery boilers or in the chemical recovery cycle were observed during the test.

In addition to the SNCR demonstration in Mönsterås, Götaverken Energy has improved the control of the combustion process by development of the air system of the recovery boiler. Table 4 shows the result from a test with this modified air system in a recovery boiler. The results show a potential NO\textsubscript{x} reduction of at least 30–40% in spite of low initial NO\textsubscript{x} level.

**TABLE 4. NO\textsubscript{x} reduction with modified tertiary air system**

<table>
<thead>
<tr>
<th>Test results from Mönsterås Oct–Nov 1990</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air system</strong></td>
</tr>
<tr>
<td>Normal</td>
</tr>
<tr>
<td>Modified</td>
</tr>
<tr>
<td>5–10% tertiary air flow of total</td>
</tr>
</tbody>
</table>

For both these methods, the resulting NO\textsubscript{x} concentration is less dependent on the amount of excess air which enables us to reduce CO (together with other minor resulting combustible compounds) with O\textsubscript{2} control as well as air control without increasing the NO\textsubscript{x} emission.

**NO\textsubscript{x}–Reduction through Combustion Control Measures**

The low NO\textsubscript{x} emissions from the recovery boiler has been attributed by, among others, Anderson and Jackson (4) to the low nitrogen content and the low heat value as well as the normal performance of the boiler with air supply on several levels. The same authors also suggest that further NO\textsubscript{x} reduction may be achieved through manipulation of air distribution and the characteristics and distribution of the fuel.

This kind of test has been carried out, within the scope of the SSVL–project Miljö 90 (5), by way of air manipulation for both temperature and distribution. None or an insignificant effect on the NO\textsubscript{x} emission of the recovery boiler has been reached without disturbing other operation parameters.
These results also correspond with Götaverken's experiences which have shown that it is possible to have a certain amount of NO\textsubscript{x} control by manipulation of a modern equipped recovery boiler. Unfortunately, the degree of manipulation is relatively limited.

To investigate if it is possible to reach more drastic effects on the NO\textsubscript{x} reduction through so called combustion control measures in a recovery boiler, a Swedish recovery boiler was equipped with some experimental air registers on different levels in the upper furnace.

The possibilities with different combinations of so called overfire air systems to reduce the NO\textsubscript{x} emission were tested on two occasions during October–November 1990.

The results were very positive and indicated a reduction of 30–40\% with a maximum performance design already at 6–8\% overfire air. Furthermore, it is likely that additional improvements can be reached if a larger amount of overfire air is being used.

The detailed results have, to some extent, been confirmed in one of Götaverken's North–American recovery boilers where a very high dry solids content has allowed a high proportion of the air provided through a simpler overfire air system.

The potential for reduction of the NO\textsubscript{x} emission of the recovery boiler with an overfire air system and with NO\textsubscript{x}\textsubscript{OUT} process respectively is indicated in the table below.

\textit{TABLE 5. Potential for NO\textsubscript{x} reduction in recovery boilers}

<table>
<thead>
<tr>
<th></th>
<th>Reduction %</th>
<th>NO\textsubscript{x} mg/MJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard System</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Overfire air system</td>
<td>30–50</td>
<td>30–40</td>
</tr>
<tr>
<td>NO\textsubscript{x}\textsubscript{OUT}</td>
<td>60–70</td>
<td>20</td>
</tr>
</tbody>
</table>

Götaverken has, through these test, participated in developing two techniques, which separately or in combination, considerably reduce the NO\textsubscript{x} emission of the recovery boiler to levels far below those which are normally reached in alternative combustion processes.
Conclusions

Compared to the energy generation sector, the emissions from kraft pulp mills are generally low. However, the recovery boiler in a pulp mill constitutes a large single source of emission because of its totally large flue gas volumes.

It has been shown that the technical potential for reduction of the different pollutants is still very high, although all the lowest limits might not be economically justified in all areas today. Table 6 shows a summary of estimated technical and economical emission target ranges for the different pollutants from a recovery boiler.

Verified results of various measures for reduction of the emissions of particles, SO₂, TRS, NOₓ and CO show that the recovery boiler has a potential to become one of the most environmentally friendly combustion processes.

**TABLE 6. Summary of emission control potentials in modern kraft recovery boilers**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Typical</th>
<th>Future</th>
<th>Control measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulates</td>
<td>mg/m³n</td>
<td>200</td>
<td>50 – 100</td>
</tr>
<tr>
<td>TRS</td>
<td>ppmv</td>
<td>0 – 5</td>
<td>0 – 2</td>
</tr>
<tr>
<td>SO₂</td>
<td>ppmv</td>
<td>50 – 300</td>
<td>0 – 50</td>
</tr>
<tr>
<td>NOₓ</td>
<td>ppmv</td>
<td>60 – 100</td>
<td>20 – 40</td>
</tr>
<tr>
<td>CO</td>
<td>ppmv</td>
<td>300</td>
<td>100 – 300</td>
</tr>
</tbody>
</table>

Dry gas at 3 % O₂
References


2. Epperly W., Broderick R., Peter–Hoblyn J.; Annual meeting of the American Power Conference April 20, 1988

3. Herngren T.; Svensk Papperstidning Nr. 15, 1989, 18–22


5. Stripple Håkan, Cooper David, Boström Curt–Åke; Miljö 90, Rapport nr 79
Figure 1. Emission of S, Na₂ and SO₂ versus furnace temperature
S/Na₂ = 30 mole-%
Figure 2. BLRBOMaster automated control package
Figure 3. Emission of SO$_2$ versus primary and secondary air flow
Figure 4. Emission of SO$_2$ versus S/Na$_2$ ratio
operating range for 65–67% DS, 100% MCR loa
Figure 5. NO\textsubscript{x} emission control technologies
Comparison of relative cost and effectiveness
Figure 6. NO$_x$-emissions from the period of start-up of the continuous run.