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ABSTRACT

Samples taken from the kraft recovery furnaces at the Georgia-Pacific Corporation's Ashdown, Arkansas mill have been analyzed for total nitrogen content. Results have been used to perform a nitrogen mass balance around the recovery furnace. 25% of the nitrogen found in the black liquor is assumed to be emitted as NO_x in the flue gas while, approximately 9% leaves the furnace in the smelt. Less than 0.1% of the black liquor nitrogen can be accounted for in some form of deposit. The remaining 66% is presumed to leave in the flue gas as molecular nitrogen (N_2).

Keywords: Black Liquor, Combustion, Deposit, Emission, Fume, Nitrogen, Nitrogen Oxides, NO_x , Recovery Furnace, Smelt.

INTRODUCTION

As mills become more concerned with NO_x emissions, it becomes increasingly important to understand as much as possible about nitrogen chemistry in a kraft recovery furnace. Ongoing student research at the Institute of Paper Science and Technology has been focused on understanding factors affecting the release of black liquor nitrogen during pyrolysis and potential *in situ* NO_x depletion mechanisms.

Nitrogen oxides (NO_x) can be formed during combustion in the presence of nitrogen. The thermal NO_x mechanism accounts for oxidation of atmospheric nitrogen (N_2). This mechanism requires extremely high temperatures which are typically not obtained during the combustion of black liquor. Several papers addressing recovery furnace NO_x emissions have concluded that the majority of NO_x is fuel NO_x , formed from the oxidation of nitrogen in the black liquor.¹⁻³ The concentration of nitrogen in black liquor solids is typically on the order of 0.1%.¹

Considering a mass balance around a recovery furnace, the exit streams consist of the flue gas, particulates, and the smelt. It has been shown that conversion of only 25% of the nitrogen in the black liquor can account for the level of NO_x measured in the flue gas from furnaces.³ Thus, the question arises as to the fate of the remaining nitrogen.

It is understood that sodium species react with SO_2 in the upper region of the furnace forming sodium sulfate (Na_2SO_4) which is captured in the electrostatic precipitators.⁴ These reactions act as a scrubbing mechanism and essentially control SO_2 emissions from recovery furnaces. It has been suggested that similar reactions could occur between sodium compounds and nitric oxide (NO) forming sodium nitrate.⁵ If such reactions do occur, one would expect to find nitrogen in furnace deposits and in particulates. It is also conceivable that similar reactions could occur between NO and the molten smelt. NO has been shown to decompose to N_2 in the presence of molten Na_2CO_3 and mixtures of Na_2CO_3 and Na_2S .⁶ In order to quantify the presence of nitrogen in these different streams, samples were taken from the two recovery furnaces at Georgia-Pacific Corporation's Ashdown, Arkansas operations.

SAMPLE SOURCE

There are currently two recovery furnaces in operation at the G-P Ashdown mill. The No. 2 Recovery Boiler is a conventional two-drum Combustion Engineering (CE)

unit. Installed in 1979, the unit was equipped with a screen superheater, economizer, and cascade direct contact evaporator (DCE). The original design burning rate was 3.5 million lbs of dry solids per day (MMlb ds/day). In 1990, the unit was upgraded by Babcock & Wilcox to a low order configuration. The DCE was replaced by a second economizer, and a third level of air delivery was added. The unit has three FD fans, two ID fans, and four oscillating liquor guns. The upgrade design conditions for the No. 2 Recovery Boiler specify a design burning rate of 4.2 MMlb ds/day with a liquor heating value of 5700 BTU/lb, as fired solids of 68%, and a steam production rate of 543,400 lb/hr at 850°F and 900 psig. The unit is currently operating around 4.0 MMlb ds/day.

The No. 3 Recovery Boiler is a 1989 single drum Götaverken boiler equipped with a large superheater and economizer. The designed burning rate is 4.5 MM lb ds/day. The unit is designed to deliver 730,000 lb steam/hr at an outlet temperature and pressure of 850 °F and 900 psig, respectively. These conditions are based on firing black liquor solids at 68% with a heating value of 6300 BTU/lb (prior to addition of saltcake and ash recycle). The No. 3 Recovery Boiler has eight gun ports and is normally fired with six stationary liquor guns. Secondary air port rodders and a larger tertiary air fan were added to the furnace in 1994. Presently, this unit operates around 4.5 MMlb ds/day.

Two sets of samples were taken from these furnaces. The first set of samples was taken from both furnaces and consisted of: black liquor feed, "as fired" black liquor, economizer deposits, ESP saltcake, and green liquor from the dissolving tank. The second set of samples was taken only from the No. 3 recovery furnace and consisted of: "as fired" liquor, smelt, weak wash, green liquor, dregs, and slaker grits. Each of these samples was analyzed for total nitrogen content. In addition, the "as fired" liquor samples were analyzed for elemental composition.

NITROGEN ANALYSIS

All samples were analyzed for nitrogen using an Antek Instruments, Inc. 7000N/S analyzer. The analyzer employs an oxygen rich combustion environment at 1100°C to convert all forms of nitrogen in the sample to nitrogen oxides which are detected by chemiluminescence. The analyzer is equipped with a multi-matrix sample inlet and is capable of measuring gas, liquid, and solid samples in the range of $\sim 2 \times 10^{-7}\%$ to 17% with a relative standard deviation of $\pm 2\%$. Analysis was conducted using the following gas flow rates for the analyzer: inlet oxygen ~ 20 cc/min, inlet helium as a carrier gas ~ 145 cc/min, oxygen to the combustion chamber ~ 365 cc/min, and oxygen to the ozone generator (for chemiluminescence detection) ~ 30 cc/min. The detector gain was set on high at a factor of 1. The instrument was calibrated using standards composed of silver nitrate in water between the concentration range 0 to 1000 ppm as N. Excellent linearity (R-Squared = 0.99993) was achieved over this range.

Solid samples were oven dried and crushed before being placed in a sample boat and weighed. The sample boat was driven into the combustion chamber by a sample drive. Solid sample sizes were approximately 10 to 20 mg. Liquid samples were injected by syringe into a sample boat containing glass wool to increase surface area for improved heat transfer and more complete combustion of the samples. All liquid samples were 5.0 μL . Due to its viscous nature, black liquor samples were weighed in sample boats at a sample size of 30 to 45 mg. A minimum of three replicates was done for each sample with the average nitrogen concentration being reported.

While this combustion method for total nitrogen measurement is relatively new, the technique provides many advantages over the wet chemical Kjeldahl method. The combustion technique offers greater safety and time savings in both sample preparation and analysis compared to the Kjeldahl method. Solids, gases, and

liquids can be analyzed to very low nitrogen levels with high accuracy and precision. With the Kjeldahl technique, only liquids and solids can be analyzed, and the accuracy for solids becomes questionable at concentrations below 0.5% N.⁷ This is considerably higher than the 0.1% N concentration typical of black liquor samples. This lack of accuracy becomes even more critical when attempting to analyze samples such as fume and smelt which have an even lower nitrogen concentration.

While the total nitrogen combustion method is more accurate and precise, additional results from using this method have shown a dependence on the sample matrix. While this may affect the accuracy, the numbers are still considered more reliable than those obtained by the Kjeldahl method. The effect of the matrix is such that the nitrogen content measured may be considerably lower than the actual nitrogen content, i.e., there may be more than 0.1% N in black liquor. Evaluation of the effect of the liquor composition on the release of nitrogen is the subject of a recent publication.⁸

RESULTS

The results of the nitrogen analysis are shown below in Tables 1 and 2. All concentrations are reported as parts per million on a weight basis. The black liquor samples are reported as ppm by weight of black liquor solids.

Table 1: Analysis of Sample Set I.

No. 2 RB	[N] ppm	No. 3 RB	[N] (ppm)
Black Liquor Feed	487	Black Liquor Feed	445
As Fired Liquor	486	As Fired Liquor	465
Economizer 1	5	Generating Bank	72
Economizer 2	7	Economizer 1	40
ESP Saltcake	27	Economizer 2	13
N. Dissolving Tank	103	ESP Saltcake	7
S. Dissolving Tank	90	Dissolving Tank	78
Green Liquor Dregs	75 - 100	Green Liquor Dregs	60

Table 2: Analysis of Sample Set II.

No. 3 Recovery Boiler	[N] (ppm)
As Fired Liquor	631
Smelt	155
Weak Wash	18
Green Liquor	88
Green Liquor Dregs	37
Slaker Grits	10

For both furnaces, the "as fired" liquor has essentially the same concentration as the black liquor feed. This indicates that any makeup chemicals or saltcake added in the mix tank do not have a significant amount of nitrogen in the liquor. The analysis of saltcake and precipitator catch confirm this assumption.

The second "as fired" liquor sample taken from the No. 3 Recovery Furnace had a significantly higher nitrogen concentration than the first (36% higher). This indicates that the wood supply or other cooking process variables can have an effect on the nitrogen content. This may ultimately affect the NO_x emissions as they are dependent on the nitrogen content of the liquor.^{9,10}

The elemental analysis of the "as fired" liquor samples is shown in Table 3.

Table 3: Elemental Analysis of Black Liquor Solids.

Component	Sample Set 1	Sample Set 1	Sample Set 2
	No. 2 RB	No. 3 RB	No. 3 RB
Carbon (C)	39.38%	38.53%	37.54%
Carbonate Carbon (CO ₃ ²⁻)	0.60%	0.54%	0.63%
Hydrogen (H)	3.68%	4.18%	3.88%
Oxygen (O)	35.95%	35.89%	36.19%
Sulfur (S)	4.31%	4.42%	4.3%
Sulfate Sulfur (SO ₄ ²⁻)	1.08%	1.26%	1.22%
Sodium (Na)	14.9%	15.1%	16.2%
Nitrogen (N)	0.049%	0.046%	0.063%

A simple mass balance has been performed around the No 3. Recovery Furnace based on the following assumptions and operating conditions:

- * Basis 100 kg dry solids
- * Solids Concentration 67%
- * Excess Air 15%
- * Reduction Efficiency 92%
- * 25% of the N in black liquor is emitted as NO in the flue gas.
- * 10% of Na in black liquor forms fume, 80% of which is captured in the ESP. The remaining 20% of the fume is deposited on the generating bank (8%), and the two economizer sections (6% each).

The results of the mass balance are depicted below in Figure 1.

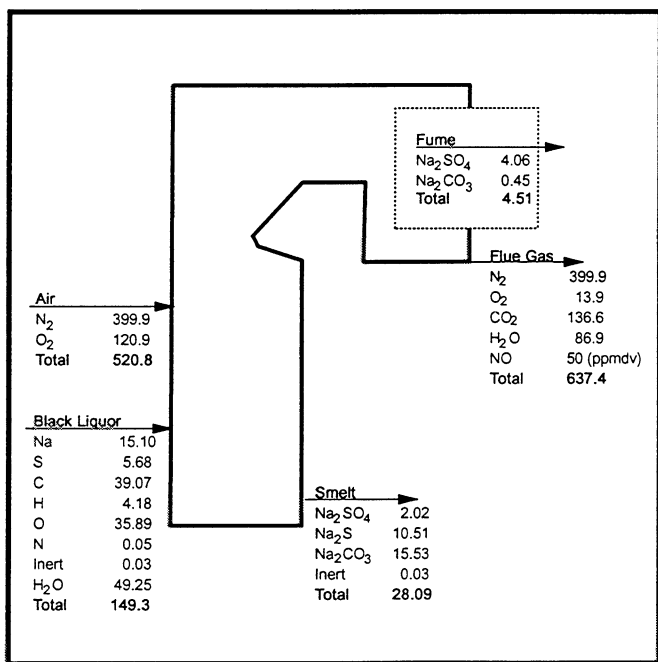


Figure 1: Mass Balance on a Recovery Furnace Based on 100 kg Dry Solids.

Based on the mass balance above and the analysis of samples taken from the furnaces, it is possible to calculate the percentage of the black liquor nitrogen that ends up in each of the exit streams. These results are shown below in Table 4.

Table 4: Nitrogen Content in Various Recovery Furnace Exit Streams.

"Exit Stream"	[N] in Stream (g N/ 10 ⁶ g)	Mass of Stream (kg)	Mass of Nitrogen (kg)	% of Input N
Generating Bank	72	0.36	25.9 x 10 ⁻⁶	0.052
Economizer 1	40	0.27	10.8 x 10 ⁻⁶	0.022
Economizer 2	13	0.27	3.51 x 10 ⁻⁶	0.007
ESP Catch	7	3.61	25.3 x 10 ⁻⁶	0.050
Smelt	155	28.1	43.6 x 10 ⁻⁴	8.71

Inspection of Table 4 shows less than 0.1% of the black liquor nitrogen can be accounted for in the electrostatic precipitator. Thus, fume scrubbing reactions (capturing N as NaNO₃) are not thought to be a significant source for the reduction of NO. It is, however, feasible that reduction reactions are occurring with fume species that give rise to gaseous products. The work of Thompson and Empie has shown that NO can be reduced to N₂ and O₂ in the presence of molten sodium carbonate (Na₂CO₃).⁶ In addition, a study at Oregon State University has shown nitric oxide can be reduced in the presence of black liquor char.¹¹

Results of the furnace mass balance indicate that approximately 9% of the nitrogen entering with the liquor leaves with the smelt. It is not clear at this point what the source of nitrogen is in smelt. It could be nitrogen from the black liquor that did not get released during combustion or it could be a reaction product that forms between NO and the inorganic salts.

Assuming that the mass flow rate of weak wash is 6.6 times the mass flow rate of the smelt,¹² calculations show 3.5 times more nitrogen leaving the dissolving tank than entering. The reason for the large difference is unknown. If the smelt concentration is actually higher by a factor of 3.5, then the amount of nitrogen leaving in the smelt corresponds to approximately 31% of the black liquor nitrogen.

Green liquor dregs had concentrations ranging from 37 to 100 ppm. Due to the low mass flow rate of dregs (on the order of 2% of the unclarified green liquor flow),¹² the dregs would not be considered a significant purge point for nitrogen.

The assumed 25% of the nitrogen emitted in the flue gas as NO_x corresponds to a flue gas concentration of 50 ppm based on dry volume. This is equivalent to approximately 30 ppm when adjusting to the common basis of ppmv at 8% O₂. Nichols *et al*, report a brief survey of NO_x emissions in the range of near zero to 120 ppmv at 8% O₂.¹

The remaining 44 to 66% is presumed to leave the furnace in the flue gas as molecular nitrogen (N₂). It should be noted that the nitrogen content of black liquor is only one of the parameters that influences NO_x emissions. Feck has reported great variability in NO_x emissions depending on the operation of the furnace.¹³

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