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ABSTRACT

Measurements have been made of the relative amounts of fuel-NO_x and thermal-NO_x in the gaseous combustion products from burning kraft black liquor in two different experimental systems. Data from the IPST black liquor reactor showed concentrations of flue gas NO_x in the range of 40-80 ppm (8% O_2 basis). Combustion using synthetic air with 21% oxygen in argon produced NO_x levels which were not statistically different from NO_x levels produced using air, indicating that all of the NO_x produced was fuel-NO_x. Using a smaller furnace, it was shown that the formation of fuel-NO_x was relatively insensitive to temperature in the range 800-1000°C. The implications from these data are that conversion of nitrogen present in black liquor to form fuel-NO_x represents a major source of total-NO_x emitted during black liquor combustion, and that increases in recovery furnace temperatures caused by increasing dry solids will not necessarily result in increased NO_x emissions. This is consistent with thermal-NO_x theory which indicates that temperatures are not high enough in black liquor combustion to form significant thermal-NO_x.

KEY WORDS

fuel-NO_x, thermal-NO_x, nitrogen oxides, emissions, black liquor, combustion, recovery furnace, pollution

INTRODUCTION

Emission of oxides of nitrogen, NO_x, from recovery furnaces has become an important environmental issue affecting the operation of recovery boilers. Since 1986, every air quality permit issued for kraft recovery furnaces has contained limits on NO_x emissions (1).

The formation of NO_x occurs primarily through two independent mechanisms, fuel-NO_x formation and thermal-NO_x formation. Fuel-NO_x is formed during black liquor combustion as a result of the oxidation of nitrogen contained in the black liquor. The important parameters affecting fuel-NO_x formation are black liquor nitrogen content and concentration of oxygen in the furnace gas. Reported compositions of numerous black liquors (2) have shown that nitrogen contents range from 0.05-0.24% (wt/wt of dry liquor solids) with an average of 0.11%.

Thermal-NO_x is formed by the oxidation of N_2 contained in the combustion air. It is the dominant source of NO_x emissions for combustion of fuels, such as natural gas, which contain little or no chemically-bound nitrogen. Thermal-NO_x formation is highly temperature dependent. However, as has been shown using thermal-NO_x formation theory (2), it seems unlikely that temperatures in recovery furnaces are sufficiently high to result in significant thermal-NO_x concentrations.

It is important to understand the relative contributions from each of these two mechanisms to the total-NO_x emitted from recovery furnaces. With the advent of high solids firing, increases in liquor solids will cause increases in both volumetric heat release rates and average temperatures in the lower furnace. Moderate increases in furnace temperature will yield order of magnitude increases in thermal-NO_x, while the effect on fuel-NO_x may be much less. Perhaps more importantly for furnaces where NO_x reduction techniques are required, the choice of control option for effective and practical reduction may be influenced by whether or not the major NO_x source is from the fuel.

It has been inferred that fuel-NO_x is the major source of NO_x for recovery furnaces (2); however, there have been no data available to verify this. The major objective of this study has been to provide quantitative measurements of the fuel-NO_x produced versus the thermal-NO_x produced during black liquor combustion.

EXPERIMENTAL METHODS

Two liquors were tested, a mill liquor and a low-nitrogen liquor. The mill liquor, obtained from the final concentrator product of a kraft pulp mill pulping softwood, contained 0.087% nitrogen (weight% of the dry liquor solids). The low-nitrogen liquor was made in the laboratory by combining appropriate amounts of reagent grade NaOH, Na_2SO_4, phenol, and dextrose with water, followed by concentration of the mixture to 65% solids in a rotary evaporator. The purpose of the low-nitrogen liquor was to provide a liquor with a nitrogen content substantially less than that of the mill liquor. The measured nitrogen level in the low-nitrogen liquor was 0.012%. Nitrogen determinations were made using Kjeldahl nitrogen analysis. Elemental compositions and heating values for both liquors are shown in Table I.

I. Liquor compositions, wt/wt% of dry solids.

	Mill Liquor	Low-nitrogen liquor
C	36.9	37.3
H	4.71	4.46
O	32.5	35.8
S	4.90	4.07
Na	18.5	18.3
N	0.087	0.012
HHV*	6,320	6,970

*higher heating value, BTU/lb solids

The mill liquor was burned in the IPST black liquor reactor, shown schematically in Figure 1. This reactor consisted of a vertical tube furnace placed above a char bed furnace. Liquor of approximately 65% solids was converted to droplets by a vibrating feed mechanism on top of the tube furnace. The droplets fell downward through upward flowing air and combustion product gases. The droplets were heated by convection from the gases and radiation from the furnace walls. Furnace wall temperatures and air preheat temperatures were as indicated in Figure 1, and were regulated by electronically-controlled electric heaters. Drying, swelling, partial pyrolysis, and limited char burning occurred as the droplets descended through the tube furnace. The swollen char particles collected in the char bed furnace, where preheated air was directed across the bed surface to complete the combustion. The air split was 50% primary and 50% secondary. The total air rate was set according to the liquor rate so as to achieve 20% excess air beyond that required for complete combustion.

A slip stream of the combustion product gases was withdrawn for continuous gas sampling. The sample was withdrawn either from the reactor exit (near the top of the tube furnace) or from various locations within the tube furnace or char bed furnace by using a stainless steel gas-cooled sampling probe. The sample stream was cooled and passed through a condenser to remove moisture and particulate. Concentrations of NO_x (both NO and NO_2) in the sample stream were measured using a chemiluminescent NO/NO_x analyzer (Thermo Environmental, Model 10AR). Preliminary test burns showed no noticeable differences between NO levels and NO_x levels, indicating that very little of the NO_x was NO_2. Concentrations of CO and CO_2 were measured using non-dispersive infrared instruments, and concentrations of O_2 were measured using a paramagnetic oxygen analyzer.

The percentage of total flue gas NO_x emissions that was formed by the oxidation of fuel bound nitrogen was determined by replacement of the combustion air with a mixture of 21% oxygen in argon. This method was adopted after the work of Pershing and Wendt (3) for fuel-NO_x measurement in coal combustion. In the absence of molecular nitrogen (N_2), the rate of formation of thermal-NO_x was effectively zero, and all NO_x formed was considered fuel-NO_x. The additional NO_x formed when air was used was due to thermal-NO_x formation. This determination of fuel-NO_x, along with knowledge of the nitrogen content of the black liquor, allowed for direct determination of the fractional conversion of liquor nitrogen to fuel-NO_x.

Tests burns were also completed using a second combustion reactor, a temperature-controlled tube furnace shown in Figure 2, to compare NO_x emitted from combustion of the black liquor to NO_x emitted from combustion of the low-nitrogen liquor and to examine the temperature dependence of fuel-NO_x. It was determined to be impractical to burn the low-nitrogen liquor in the black liquor reactor due to the uncharacteristic manner (i.e., unlike the mill liquor) in which the low-nitrogen liquor swelled and burned.

For burns in the tube furnace, a ceramic boat was loaded with approximately 300 mg of liquor (200 mg of liquor solids) and placed in the end of the tube furnace. Air was drawn through the tube furnace at 5 slpm which flow rate provided approximately one-second of residence time for the gases in the tube. The burn time was 2 minutes, which was sufficient for complete combustion of the organic components in the boat. The excess air level in these tests was much greater than 20%, as 10 liters of air is several times that (approximately 10 times) required for complete combustion of 200 mg of solids. Furnace temperature was varied between 800°C and 1000°C.

Combustion products were drawn out of the tube furnace, cooled and filtered, and NO_x was measured using the chemiluminescent analyzer. The NO_x level was recorded on a strip chart and the area under the curve determined by integration to give the total-NO_x emitted during the course of the burn. This was converted to a concentration by knowing the initial mass of the liquor solids in the ceramic boat and the air requirement for complete combustion of the solids (4.6 grams of air required per gram of liquor solids).

All NO_x concentrations are reported on the basis of ppm (volume) adjusted to 8% O_2 in the dry flue gas. This basis was chosen as it is frequently used for reporting measured flue gas emission levels and it is often used in permits and regulatory statements.

CONCLUSIONS

The major conclusions supported by these data are that during black liquor combustion: (1) conversion of nitrogen in black liquor to fuel-NO_x is a major source of recovery furnace NO_x; (2) the formation of fuel-NO_x is relatively insensitive to temperature in the range 800-1000°C; (3) higher levels of liquor nitrogen are expected to yield higher NO_x levels for the same combustion conditions; (4) nitrogen evolves from the liquor solids during both devolatilization and char burning; (5) NO_x is formed during both in-flight burning and char bed burning; and (6) noticeable decay of NO_x can occur after a maximum NO_x concentration has been reached.

ACKNOWLEDGEMENTS

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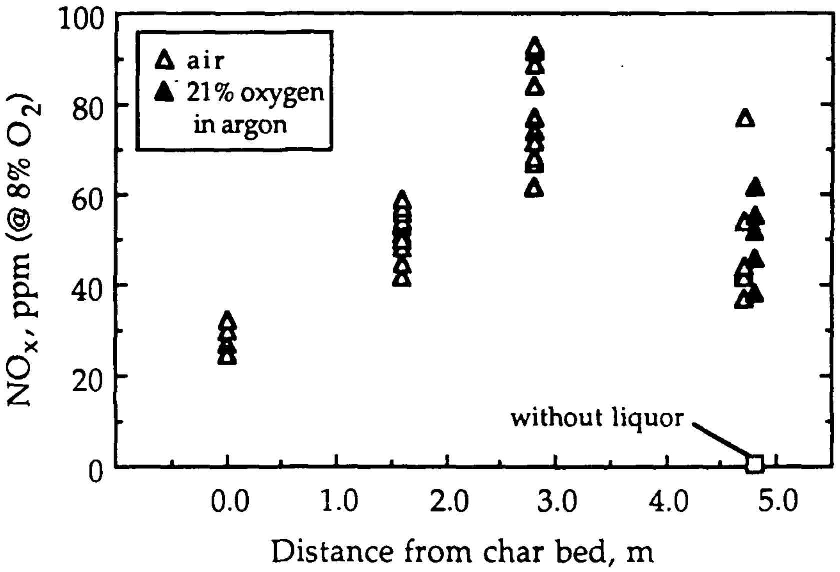
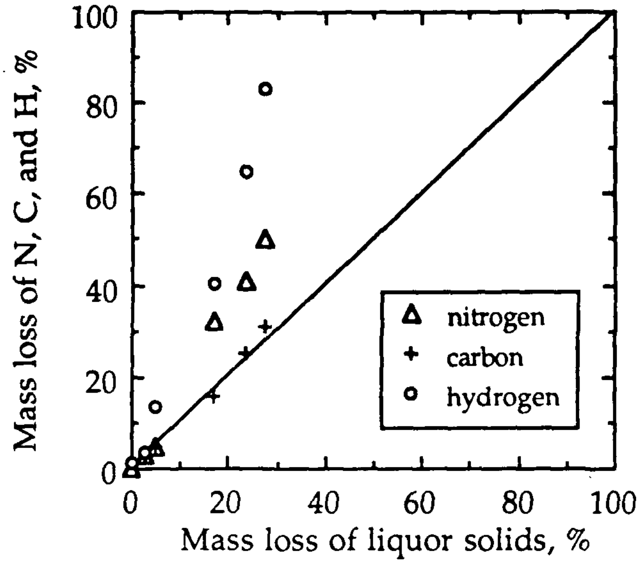
3. NO_x emissions from combustion of mill liquor in black liquor reactor.



4. Relative volatilities during pyrolysis of mill liquor in covered crucibles at 700°C.



5. NO_x measurements from combustion of liquors in the tube furnace.