Nitrogen oxide emissions from a kraft recovery furnace

Alan L. Prouty, Richard C. Stuart, and Andre L. Caron

ABSTRACT: Nitrogen oxide (NO_x) emissions from a rebuilt kraft recovery furnace slightly exceeded the specified limit of 1.1 lb/ton (0.55 kg/metric ton) of black-liquor solids. Mill trials were undertaken to determine whether NO_x emissions could be minimized by modifying furnace operation. NO_x emissions increased when secondary air was shifted to tertiary ports. NO_x emissions fell when the amounts of primary and total air were decreased, but this increased emissions of other pollutants. After demonstrating that best operation of the furnace could not meet the permit limit for NO_x emissions, the mill received a new permit with an emissions limit that matched the furnace's performance at best operation.

KEYWORDS: Air, carbon monoxide, combustion, emission, emission standards, evaluation, nitrogen oxides, recovery furnaces.

James River Corp. proposed a major energy and recovery modernization project for its mill in Camas, WA, in 1988. A key element of the project was the rebuild of a 1956 Babcock & Wilcox kraft recovery furnace to increase its firing capacity to 1.9 million lb (0.86 million kg) of solids per day. The air permit obtained for the rebuild identified boiler design and operation as the best available control technology for control of nitrogen oxides (NO_x). A NO_x emission rate of 1.1 lb/ton (0.55 kg/metric ton) of virgin black-liquor solids (BLS) was adopted based on published emissions data (*1, 2*).

Performance testing done after completion of the project showed NO_x emissions of 1.17 lb/ton (0.58 kg/metric ton) BLS. Therefore, the mill initiated a project to study NO_x emissions from kraft recovery furnaces. The project goals were to identify operational techniques for controlling NO_x and to determine whether emissions could be reduced using any of these techniques.

NO_x formation in recovery furnaces

The formation of NO_x during combustion occurs by two mechanisms:

- Fuel NO_x—oxidation of fuel-bound nitrogen
- Thermal NO_x—oxidation of nitrogen present in the combustion air.

The formation of fuel NO_x is primarily dependent on fuel nitrogen content, fuel properties, temperature, and the stoichiometric conditions present during combustion. The major variables influencing the formation of thermal NO_x are flame temperature, oxygen content in the flame zone, and gas residence time at high temperature, which is determined by the configuration of the combustion unit. The degree of thermal NO_x formation tends to increase with temperatures above approximately 2400°F (1300°C), particularly when the oxygen concentration in the combustion zone is 2% or greater (*3*).

It is believed that the majority of NO_x emitted from recovery furnaces is the result of fuel NO_x formation (*4*). However, as will be seen in this work, peak combustion temperatures sometimes exceed 2400°F, so it is likely that some thermal NO_x also is formed. At this time, it is unclear what portion of the emitted NO_x is attributable to thermal NO_x formation.

NO_x emissions from older kraft furnaces with direct-contact evaporators have traditionally been low compared with fossil-fuel-fired boilers. The lower NO_x emissions were a function of furnace design and operation mode. Temperatures in the hearth were usually below 2100°F because of the high levels of moisture in the liquor being fired and because of either excessive or inadequate char bed cover. Furthermore, black liquor with a high moisture content (33–40%) limits flame temperature. NO_x emissions were typically in the range of 30–65 ppm (*1, 2*).

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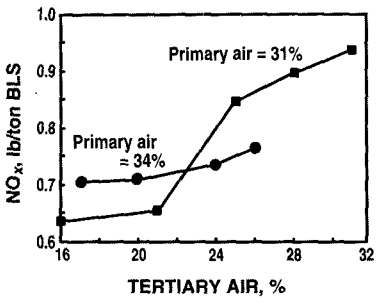
I. Characteristics of virgin black liquor*

Component	*Content, %*
Solids	71.82
Ash	35.36
Carbon	37.07
Oxygen	33.54
Sodium	18.25
Sulfur	4.48
Hydrogen	3.55
Potassium	1.54
Chlorine	0.64
Nitrogen	0.12

*Gross heating value = 6110 Btu/lb

1. NO_x emissions as a function of tertiary air



II. NO_x and CO emissions at various levels of primary air*

Primary air, %	*NO_x, lb/ton of BLS*	*CO, ppm (at 8% O_2)*
34	0.71	135
31	0.64	...
28	0.62	236
25	0.60	301

*Tertiary air held constant at 16% of total air flow

The advent of the low-odor recovery furnace has led to furnace operating conditions that produce higher NO_x emission rates. Black-liquor solids are typically in the range of 70–73%, resulting in higher flame temperatures. Also, excess air is maintained at a higher level in an effort to maximize the conversion of total reduced sulfur (TRS) compounds to sulfur dioxide. NO_x emissions from low-odor furnaces range from 77 ppm to 140 ppm (*5–7*), depending on the moisture content of the black liquor, the amount of excess oxygen in the combustion gas, and the air distribution.

NO_x control strategies

Control strategies for NO_x emissions fall into one of three categories: precombustion control, combustion modification, or postcombustion controls (*8, 9*).

Precombustion controls include changing of fuels and increasing the moisture content of the fuel being burned. Combustion control techniques are quite varied. They include firing with low excess air, staged air combustion, staged fuel combustion, flue gas recirculation, water injection, and low-NO_x burners. Common postcombustion control techniques include noncatalytic reduction by ammonia and urea injection and reduction with ammonia over catalysts.

Most of these control techniques are impractical or have not been demonstrated in a kraft recovery furnace (*10*). The two control strategies that offered the greatest potential for reducing NO_x emissions were

- Optimizing staged-air combustion
- Firing with low excess air.

Trials were undertaken to evaluate these control techniques.

Experimental procedures

Each trial was run for a time period of 3–6 h. Only the data collected for one hour after the furnace operating conditions had been adjusted were used for the purposes of this study. Unless specified otherwise, combustion air flows were adjusted to maintain the oxygen content in the generator section at 1.5%.

Flue-gas characteristics were measured using continuous emission monitors for NO_x, CO, TRS, and oxygen. Temperatures at the level of the liquor gun in the recovery furnace were measured using a radiometer from E^2 Technology.

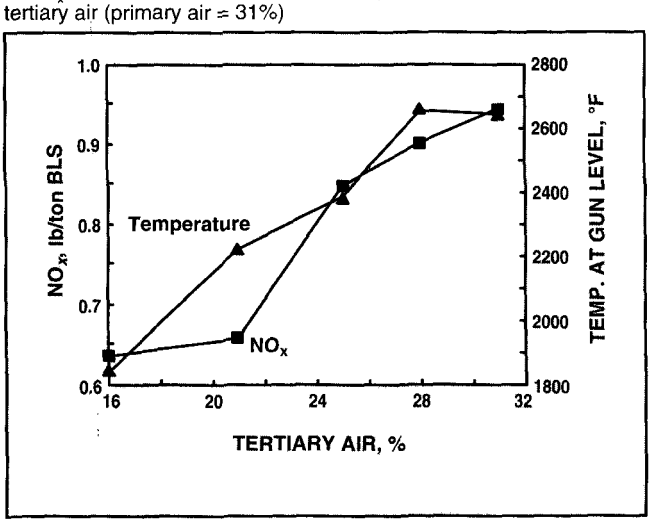
One-hour averages of furnace operating conditions (air flows, temperatures, firing rate) were measured for each trial. Samples of virgin and as-fired black liquor were taken during each trial. The samples were analyzed for solids, ash, heating value, and elemental composition (C, O, Na, S, H, K, Cl, N). Average characteristics for the virgin black liquor are listed in **Table I.**

The liquor nitrogen content remained constant throughout the trials. As-fired liquor typically had a heating value of 5930 Btu/lb, solids of 73.4%, and ash content of 36.9%. Except where noted otherwise, all emissions were calculated on an as-fired liquor basis.

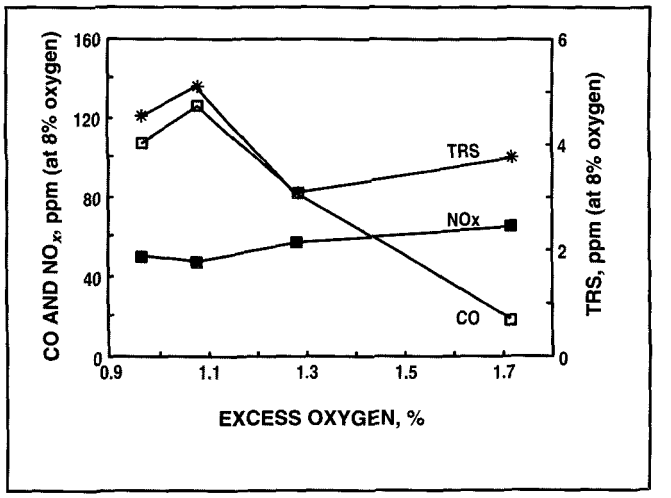
Results and discussion

Several aspects of furnace operation were examined for their influence on NO_x emissions. The concept of staged combustion was investigated by observing the effect of shifting air among the three air ports (primary, secondary, and tertiary) on NO_x emissions. The effect of excess air on NO_x emissions was determined by varying the oxygen content in the combustion gases. These trials were conducted while firing 1.44 million lb (0.65 million kg) of liquor solids per day (75% of capacity) for ease of operation. Other trials were run to investigate the influence of firing rate on NO_x emissions. Finally, a few runs were conducted at the design firing rate to see what differences existed in NO_x emissions between operation at 75% design capacity and 100% design capacity.

2. NO_x emissions and temperatures at liquor-gun level as functions of tertiary air (primary air = 31%)



3. Emissions of several pollutants as a function of excess oxygen in combustion gas



III. NO_x emissions at various liquor firing rates*

Firing rate, gal/min	*NO_x, ppm (at 8% O_2)*
115	43
125	45
165	57
170	59
200	65

*Oxygen in generator section maintained at 1.4–1.6%

Staged combustion

The staged-air concept was evaluated by conducting three sets of trials that involved shifting combustion air among the three furnace zones. All of these trials were conducted at a black-liquor firing rate of 125 gal/min (1.44 million lb solids per day). Two sets of trials involved holding the amount of primary air steady and shifting air from the secondary to the tertiary levels. Another trial involved shifting primary air to the secondary ports and holding the amount of tertiary air constant. Oxygen in the combustion gas in the generator section was maintained at 1.5% for all trials.

For the first trial set, the percentage of air going through primary air ports was held constant at 34% of the total air flow of 278,000 lb/h (126,000 kg/h), and secondary air was shifted to tertiary ports. Results from this set of trials indicated that a low amount of tertiary air (16%) gave the lowest NO_x emissions, as seen in **Fig. 1**.

During the second set of trials, tertiary air was held constant at 16% of the total air flow of 278,000 lb/h, and primary air was shifted to secondary ports. While decreasing the amount of primary air did result in lower NO_x emissions, CO emissions increased significantly, as seen in **Table II**. Smelt reduction efficiencies ranged from 85% at 34% primary air to 92% at 25% primary air. The results of this set of trials indicated that an optimum amount of primary air was 31% of the total air flow.

For the third set of trials, air flow through the primary ports was held constant at 31% of the total air flow of 273,000 lb/h, and secondary air was shifted to tertiary ports. Once again, the NO_x emissions increased as air was shifted to the tertiary ports, as seen in Fig. 1. This effect was more dramatic at 31% primary air than at 34% primary air. The conclusion following these three trials was that the optimum air distribution for minimizing NO_x and CO emissions was 31% primary, 53% secondary, and 16% tertiary.

To better understand these test results, it is helpful to review the manner in which combustion air at the three different levels influences the combustion processes. Primary air is intended to supply just enough oxygen to maintain the reducing environment at the char bed surface while creating combustibles and burning out char carbon. Secondary air has several functions—drying and devolatilization of the liquor droplets, char combustion, and control of SO_2, TRS, and CO levels in the combustion gas. Tertiary air supplies the oxygen needed to complete combustion of the organics liberated from the char bed and to oxidize the TRS gases.

Published information shows that the temperature profile of a kraft recovery furnace ranges from approximately 1800°F (980°C) at the bed surface to more than 2400°F (1315°C) at a point between the secondary air ports and the liquor guns. Temperatures then decrease to about 1000–1100°F (540–590°C) at the entrance to the generator section (*11–13*). The objective of staged combustion is to reduce peak combustion temperature and thus lower NO_x formation. We hypothesized that shifting air from the secondary to tertiary air ports would increase the length of the combustion zone while reducing the peak combustion temperature. This, in theory, would lead to lower NO_x emissions.

As Fig. 1 showed, shifting air from the secondary to the tertiary ports led to increased NO_x emissions. This can be explained by the temperatures at the liquor-gun level, as seen in **Fig. 2**. As the amount of tertiary air increased,

so did the temperature at the liquor gun level. This would indicate that shifting secondary air to the tertiary ports tends to increase the destruction of organics at or near the liquor-gun level. Consequently, the goal of reducing peak temperatures by shifting more of the organics combustion to the upper portion of the furnace (above the gun liquor level) was not achieved by increasing the amount of tertiary air.

The reduction in NO_x formation and subsequent increase in CO emissions when the primary air was reduced indicates that the amount of primary air critically affects pollutant emissions. Therefore, the lower portion of the furnace (between the primary and secondary air ports) can be a significant source of either NO_x or CO formation, depending on the amount of primary air supplied.

Firing with low excess air

One set of trials involved reducing the total amount of combustion air in the furnace while maintaining the same proportion of air to each of the three levels of ports. **Figure 3** shows that NO_x emissions decreased by approximately 30% as the excess oxygen concentration in the combustion gas was reduced from 1.7% to 1.0%. However, emissions of CO increased five-fold. The results indicate that the practice of firing with low excess air to restrict NO_x formation is limited by the tradeoff between the formation of NO_x and other pollutants such as CO and TRS. This phenomenon has also been observed in other work (*14*).

Firing rate

NO_x emissions climbed steadily as the firing rate increased, as seen in **Table III**. There are two possible explanations for the increase in emissions. Obviously, the introduction of additional liquor means that there is more fuel nitrogen available to form fuel NO_x. In addition, an increase in the firing rate could increase the temperature to the point that it would become a factor in the formation of thermal NO_x.

Emissions at design firing rate

Several trials were run in which air was shifted among the various levels while firing at the design rate of 1.9 million lb/day. The same trends observed at the lower firing rate held true at the design firing rate. NO_x emissions increased when tertiary air was increased and decreased when primary air decreased. However, the change in emissions was not very significant, indicating that staged combustion is not an effective strategy for reducing NO_x emissions at design firing rate. Typical NO_x emission rates measured over a 24-h period while firing at design rate were 1.20–1.30 lb/ton of virgin BLS.

Summary

Two techniques for controlling NO_x emissions were investigated: staged-air combustion and firing with low excess air. Results showed that both strategies are of limited effectiveness in controlling NO_x emissions.

Operating with a minimum of primary and tertiary air gave the lowest NO_x emission rates. NO_x emissions were also reduced by limiting the total amount of combustion air. However, reducing the amount of primary air and total air increased CO emissions. Obtaining the proper balance of air distribution and the amount of combustion air is crucial in controlling emissions of NO_x, CO, and other pollutants.

The results of this project were presented to the Washington Department of Ecology to show that best operation of the recovery furnace could not meet the permit limit. As a result, the NO_x emission limit was raised to 1.3 lb/ton of virgin BLS.

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