Effect of stripper off-gas burning on NO_x emissions

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ABSTRACT: We conducted tests to: (1) determine the ammonia content of kraft pulp mill condensates sent to steam strippers; (2) quantify the efficiency of steam strippers for stripping ammonia from condensates; (3) determine the amount of NH_3 in stripper off-gases (SOGs) oxidized to NO_x in lime kilns, boilers and thermal oxidizers; and (4) correlate any NO_x emission increases to operating parameters such as combustion temperature and oxygen level in the combustion zone. The ammonia content of the condensates in the study ranged from 94 mg/L to 508 mg/L. The strippers removed essentially all of the ammonia from the condensates. The amount of ammonia in the SOGs that was oxidized to NO_x ranged from 6.3% to 34.4%, with an average of 19.7%. Apparently, the amount of ammonia converted to NO_x was not related to the type of combustion device. The increase in NO_x emissions due to SOG burning ranged from 0.25 to 2.76 pounds/thousand gallons of condensate stripped (KGCS) and averaged 1.13 lb/KGCS. At the mills tested, this corresponds to NO_x emissions increases ranging from 4.7 lb/hr to 49 lb/hr. Tests at a limited number of facilities showed that the fraction of ammonia that was not converted to NO_x did not leave the stack as ammonia, which suggests that the ammonia not oxidized to NO_x was reduced to molecular nitrogen.

Application: Kraft mill environmental personnel will find this useful for estimating the amount of NO_x emissions that would occur from the combustion of condensate stripper off-gases.

In the kraft process, some of the nitrogen that is naturally present in wood chips is reduced to ammonia during pulping [1,2]. Since the pH of black liquor is high, the solubility of ammonia in black liquor is low, and the ammonia dissolved in black liquor is released with the vent gases from digesters and evaporators. As the digester and evaporator vent gases are condensed prior to thermal oxidation, some of the ammonia ends up in the condensates. If a mill uses a steam stripper to strip TRS and volatile organics from the condensates, the ammonia in the condensates is also stripped and becomes a part of the stripper off-gases (SOGs).

Kymalainen et al. [1] reported that the stripping of foul condensates is the main point of ammonia exit from the recovery process, and that the amount of ammonia nitrogen in the SOGs is comparable to the NO_x emissions from a recovery furnace. A 1992 NCASI study reported that the NO_x emissions from recovery furnaces average 2.3 lb/ton, which translates to 420 tons/year of NO_x for a 1000 tons/day mill. This suggests that if there is stoichiometric conversion of SOG ammonia to NO_x when these gases are thermally oxidized, there is a potential for significant NO_x increases from a mill when it installs a steam stripper and thermally oxidizes the resulting SOGs. However, it was not known how much of the ammonia in the SOGs would be converted to NO_x in the various combustion devices used for SOG combustion, i.e., thermal oxidizers, lime kilns and power boilers.

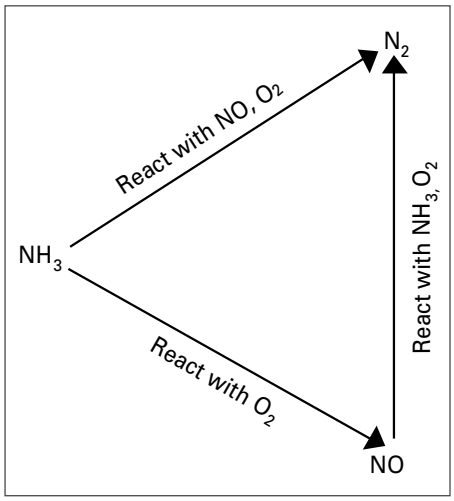
When SOGs are incinerated in various combustion devices, it is expected that at sufficiently high temperatures some of the ammonia contained in these gases could be oxidized to NO_x. In the selective non-catalytic reduction (SNCR) technique for NO_x reduction, ammonia or urea is injected into flue gases within a certain temperature window (typically 1600°F to 2100°F). Above this temperature window, the NH_3 is expected to partially oxidize to NO. Below this window, the NH_3 is expected to remain partially unreacted. Both situations are undesirable. Kraft mill SOGs, which contain ammonia, are typically introduced into the hot flame zone of a combustion device, such as a lime kiln, power boiler or dedicated thermal oxidizer. Many thermal oxidizers operate with combustion chamber temperatures below about 1600°F, making it likely that much of the NH_3 in the SOGs treated in these oxidizers will not be oxidized to NO_x. However, it is important to keep in mind that the flame temperature at the point of introduction may be hotter than the measured combustion chamber temperature. Power boilers and lime kilns typically have hotter combustion zone temperatures than thermal oxidizers, which could possibly result in higher ammonia-to-NO_x conversions when SOGs are burned in these devices. Thus, the initial temperatures experienced by the NH_3-containing SOGs are probably on the order of 2000°F to 3000°F. Ammonia is expected to be destroyed at these temperatures by two competing mechanisms, one involving the oxidation of NH_3 to NO in the presence of O_2 and the second involving the reduction of NH_3 to N_2 by reaction with NO (the SNCR reaction).

Several investigators have described the overall reactions occurring in the SNCR process by two competitive (for NH_3) or successive (for NO), essentially irreversible reactions [4,5] as shown below.

$$NH_3 + NO + \frac{1}{4}O_2 \rightarrow N_2 + \frac{3}{2}H_2O \quad (1)$$

$$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O \quad (2)$$

These reactions are illustrated in **Fig. 1**. NH_3 entering the combustion device can either react with O_2 to form NO, or it can react with NO and O_2 to form N_2. And, NO formed from the reaction of NH_3 with O_2 can react with NH_3 and O_2 to form N_2. The factors that affect the out-



1. Reactions of ammonia and nitric oxide

come of the reactions of ammonia and nitric oxide include: temperature, residence time, oxygen concentration, concentrations of NH_3 and NO, and the presence of other compounds [6].

At the initiation of this study, the limited data that were available to NCASI regarding NO_x emissions from the burning of SOGs in dedicated thermal oxidizers suggested that while the presence of SOGs could lead to increased NO_x emissions, the increase was much less than that corresponding to complete conversion of ammonia to NO_x. Because of the uncertainty associated with NO_x generation as a result of SOG burning and recognizing that a number of mills were considering installing steam strippers to comply with the Cluster Rule, in 1998 NCASI initiated a study to examine the issue of NO_x formation from combustion of ammonia in stripper gases. The specific objectives of the study were to:

1. Determine the effect of SOG burning on NO_x emissions from thermal oxidizers, lime kilns, coal-fired boilers and combination coal/wood-fired boilers.
2. Determine the conversion of SOG ammonia to NO_x in the various combustion devices.
3. Determine the fraction of the total nitrogen in SOGs that ammonia typically composes.
4. If possible, perform nitrogen material balances around the combustion devices.
5. If possible, relate the amount of ammonia converted to NO_x to combustion unit operating parameters such as temperature and post-combustion percent oxygen.

The following results are summarized from the complete study results published in NCASI Technical Bulletin No. 802 [3].

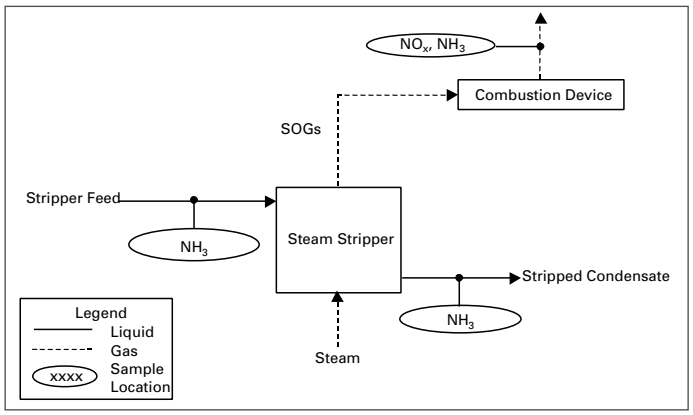
METHODOLOGY AND TEST PLAN

As shown in **Figure 2**, the effect of SOG burning on NO_x emissions was quantified by measuring the NO_x emissions from the combustion device with and without introduction of SOGs. Concurrent with the NO_x testing, samples of the foul condensate feed to the stripper and the stripped condensate were collected and analyzed for ammonia content. From these values, the amount of ammonia in the SOGs was calculated via material balance. From the amount of ammonia in the SOGs and the amount of NO_x increase from burning the SOGs, the amount of ammonia converted to NO_x in the combustion device was calculated. The combustion units tested as part of this study included three thermal oxidizers, two coal-fired power boilers, one combination wood- and coal-fired power boiler, and two lime kilns (one gas-fired and one oil-fired).

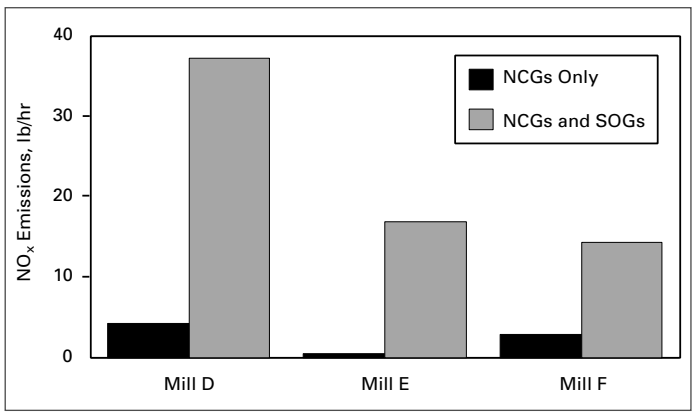
An instrumental NO_x analysis method, similar to EPA Method 7E, was used to continuously measure NO_x emissions during the test period. The ammonia content of the stripper feed and stripped condensate streams was determined by sample collection through a cooling coil, followed by sample preservation with sulfuric acid and analysis via ion chromatography. Ammonia in the stack emissions was determined via sampling with an aqueous impinger method followed by analysis of the impinger catch via ion chromatography. The details of this method are explained in NCASI Technical Bulletin No. 789 [7].

CONDENSATE STRIPPER AND SOG TEST RESULTS

Tests were conducted to determine the ammonia content of kraft pulp mill condensates sent to steam strippers, and quantify the efficiency of steam strippers for stripping ammonia from condensates. At each of the seven mills in this study, the condensate stream sent to the steam stripper contained significant levels of ammonia. The ammonia content of stripper feed streams ranged from 94 mg/L to 508 mg/L, and the stripper feed flow rates were found to range from 160 gal/min to 515 gal/min. In all cases, the ammonia was entirely or almost entirely



2. Sample collection locations



3. Thermal oxidizer NO_x emissions

stripped from the stripper feed stream and became part of the SOGs sent to the combustion device. The amount of ammonia sent to the combustion devices as part of the SOGs ranged from 0.70 to 3.33 lb/KGCS (thousand gallons of condensate stripped). In addition to the ammonia analysis, condensate samples were also analyzed for total Kjeldahl nitrogen (TKN). For the condensate samples analyzed in this study, the ammonia concentration (as nitrogen) averaged 91% of the TKN concentration.

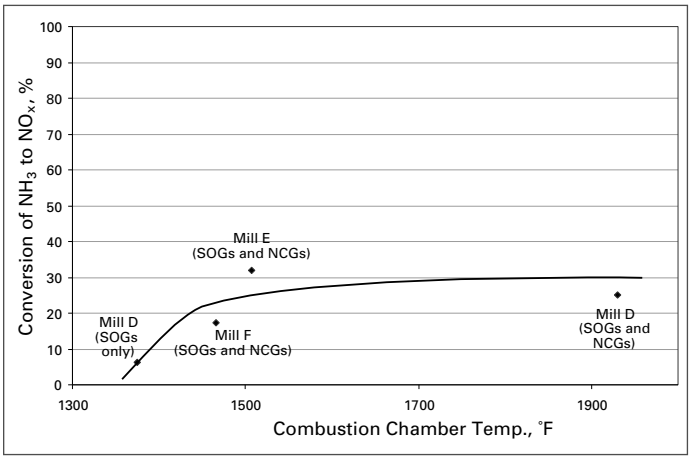
THERMAL OXIDIZER RESULTS

The NO_x emissions from three thermal oxidizers while burning only LVHC NCGs, and while burning both LVHC NCGs and SOGs are shown in **Fig. 3**. The NO_x emissions from the thermal oxidizers while burning only LVHC NCGs ranged from 0.6 lb/hr to 2.9 lb/hr. The low NO_x emissions from the Mill E thermal oxidizer while burning only LVHC NCGs may be related to the relatively low combustion chamber temperature, which was 1261°F versus about 1500°F at the other two thermal oxidizers. When both LVHC NCGs and SOGs were burned, the NO_x emissions ranged from 14.3 lb/hr to 37.4 lb/hr and averaged 22.9 lb/hr. The increase in NO_x emissions from adding SOG burning to LVHC NCG burning ranged from 1.14 to 2.76 pounds/thousand gallons of condensate stripped (lb/KGCS) and averaged 1.87 lb/KCGS.

The Mill D results suggest temperature may play a role in the conversion of SOG ammonia to NO_x. When the SOGs were burned alone, the average combustion chamber temperature was 1375°F, and the conversion of ammonia to NO_x was 6.3%. When the SOGs were burned with the LVHC NCGs, the average combustion chamber temperature rose to 1930°F and the average conversion of ammonia to NO_x was 25.2%. The increase might have been due entirely to thermal NO_x, but this does not seem likely since the percentages of ammonia converted to NO_x at the Mills E and F thermal oxidizers were 31.9% and 17.3%, respectively, at the much lower temperatures of 1507°F and 1466°F.

The peak flame temperature is expected to be much higher than the combustion chamber temperature. The kinetics for the reactions of NH_3, NO and O_2 suggest that for 17% to 32% ammonia-to-NO conversion to occur, the flame temperature at the point of SOG introduction was hotter than the measured combustion chamber temperature. In **Fig. 4**, the percentages of ammonia-to-NO_x conversion are plotted versus the combustion chamber temperatures. From the limited amount of data, it appears that the ammonia to NO_x conversion increases with temperature up to a combustion chamber temperature of about 1500°F to 1600°F, and then levels out in the range of 25% to 30% conversion. Once combustion chamber temperatures have reached 1500°F to 1600°F, further increases in combustion chamber temperature may not translate to significantly hotter peak flame temperatures. If this is the case, then further increases in combustion chamber temperature would not be expected to increase the amount of ammonia converted to NO_x.

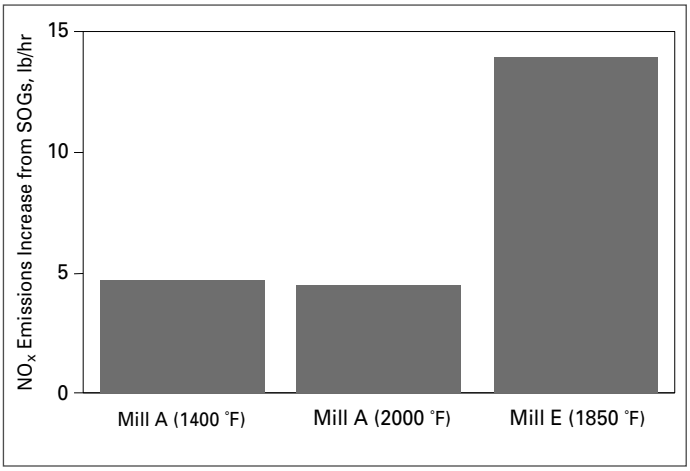
In general, the thermal oxidizer stack oxygen and NO_x levels fluctuated too much and too rapidly to develop a relationship between NO_x emissions and the stack oxygen level. Additionally, there were essentially no data available at stack oxygen levels of less than 6%. At Mill D, an attempt was made to relate stack oxygen levels, in the range of 6% to 10%, to NO_x emissions during the combined combustion of LVHC NCGs and SOGs. However, no apparent relationship was found.



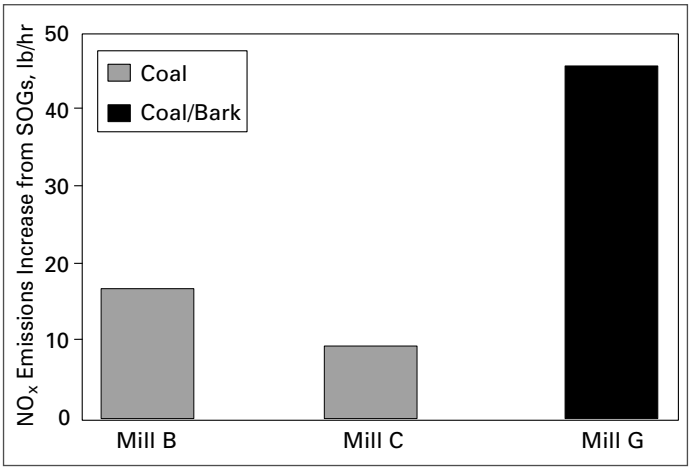
4. Conversion of NH_3 to NO_x as a function of thermal oxidizer combustion chamber temperature

LIME KILN RESULTS

The amounts of the NO_x emissions increases from SOG burning in the lime kilns at Mills A and E are summarized in **Fig. 5**. The lime kiln at Mill A was tested at low and high temperatures, and the results from the two temperatures are presented separately. Burning SOGs in the lime kilns resulted in NO_x emissions increases of 4.7 lb/hr to 13.9 lb/hr. The percentages of ammonia converted to NO_x were 12.3% at Mill A–low temperature, 10.8% at Mill A–high temperature and 23.3% at Mill E. The ammonia converted to NO_x was about twice as high in the Mill E lime kiln as it was in the Mill A lime kiln. This could be related to the fact that the Mill A lime kiln fuel was natural gas, whereas the Mill E lime kiln burned fuel oil. It also could be related to other operational factors that may affect the temperature, oxygen level, and/or the nitric oxide level in the area where ammonia is participating in reactions with oxygen and nitric oxide. Additionally, the efficiency with which the SOGs are mixed into the combustion gases, and the presence of other compounds could be related to the different percentages of ammonia converted to NO_x in the two kilns. The conversion of ammonia to NO_x at Mill E was about twice as large as it was at Mill A, as was the average post-combustion zone oxygen level. This suggests that the ammonia-to-NO_x conversion in lime kilns might be related to the kiln post-combustion zone oxygen level. However, analysis of the data from the Mill E lime kiln did not indicate a relationship between the post-combustion zone oxygen level and NO_x emissions. The results from the lime kiln at Mill A suggest that, for lime kilns, the conversion of ammonia to NO_x is not dependent on the dry-end lime bed temperature. Thus, for the lime kilns, neither oxygen nor temperature could be identified as having an effect on the conversion of ammonia in the SOGs to NO_x.



5. NO_x emissions increases from burning SOGs in lime kilns



6. NO_x emissions increases from burning SOGs in boilers

POWER BOILER RESULTS

The increases in NO_x emissions from burning SOGs in power boilers at Mills B, C and G are shown in **Fig. 6**. These increases were 17 lb/hr, 10 lb/hr and 49 lb/hr, respectively. The percentages of ammonia oxidized to NO_x were 27.5%, 7.5% and 34.4%, respectively. The boilers at Mills B and C were coal-fired, whereas the boiler at Mill G was a combination coal- and wood-fired boiler with 51% of the heat input from wood. At all three of these boilers, the SOGs were injected in the flame zone. The combination boiler at Mill G would be expected to have had the lowest temperature in the flame zone, yet it had the highest conversion of ammonia to NO_x. Thus, it would seem that temperature in the flame zone did not affect the conversion of ammonia to NO_x.

It is possible that the post-combustion zone oxygen level could have played a role in the conversion of ammonia to NO_x. The average post-combustion zone oxygen levels were 3.7%, 3.5% and 6.1% at Mills B, C and G, respectively. Winter et al. [8] state that 6% oxygen in the post-combustion zone is typical for commercial wood-fired boilers. This is significantly higher than the typical oxygen level utilized for fossil fuel-fired boilers (3% to 4%). Thus, the higher oxygen levels found in wood-fired boilers may result in higher conversions of ammonia to NO_x in wood-fired and combination wood-fired boilers than in fossil fuel-fired boilers.

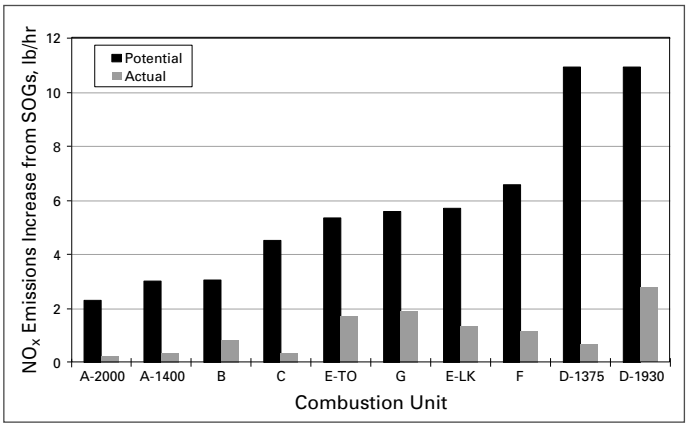
At the Mill C boiler, the conversion of ammonia to NO_x was only 7.5%, despite the fact that the SOGs were injected in the midst of the pulverized coal injection levels. It would undoubtedly be very hot in this zone, which would lead one to expect a relatively high conversion of ammonia to NO_x. Perhaps, however, the rapid consumption of oxygen by the fuel in this zone did not permit enough oxygen to be available for a significant, net conversion of ammonia to NO_x.

CONVERSION OF SOG AMMONIA TO NO_x

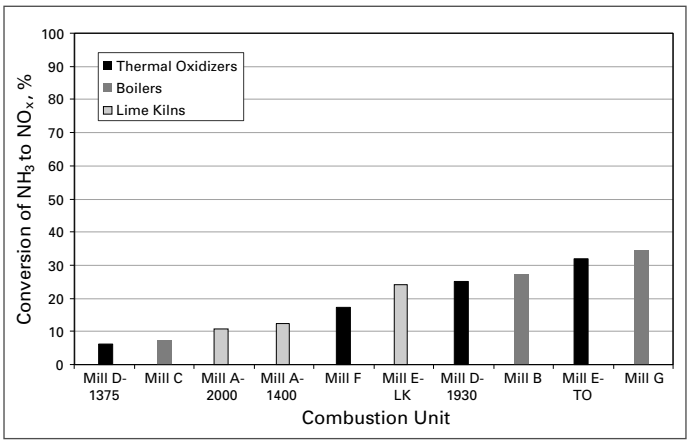
The amount of ammonia converted to NO_x was calculated from the NO_x emissions with and without SOG burning, the flow rate of the stripper feed, and the concentrations of ammonia in the stripper feed and stripped condensate. The steam strippers were very efficient at removing ammonia, and the concentrations of ammonia in the stripped condensates were generally close to or below the non-detect level. The stripper feed flow rates for the units tested in this study ranged from 110 gal/min to 515 gal/min. Thus, in **Fig. 7**, the amounts of potential and actual NO_x emissions increases are shown on a per gallon of condensate stripped basis. The "potential amount" is the amount of the NO_x emissions increase that would occur if all of the ammonia in the SOGs was oxidized to NO_x. The "actual amount" is the amount of NO_x emission increase measured at the combustion unit. The amounts of ammonia sent to the combustion devices with the SOGs ranged from 0.70 to 3.33 lb NH_3 as nitrogen/KGCS. This would correspond to a potential of 2.3 to 11.0 lb NO_x/KGCS, if it all converted to NO_x in the combustion device. The actual NO_x increases ranged from 0.25 to 2.76 lb/KGCS. As shown in **Fig. 8**, the percentages of ammonia converted to NO_x ranged from 6.3% to 34.4% for the three thermal oxidizers, two coal-fired boilers, one combination wood/coal-fired boiler and two lime kilns tested in this study. The magnitude of the conversion percentage apparently was not related to the type of combustion device.

FATE OF UNOXIDIZED AMMONIA

At one thermal oxidizer, one lime kiln and one coal-fired boiler, tests were conducted to determine if any unreacted ammonia was leaving the combustion devices. No significant amounts of ammonia were found in the emissions from any of these combustion devices. For the flame zone temperatures in the boiler and lime kiln, this is consistent with the theoretical kinetics. At the combustion chamber temperatures reported for thermal oxidizers, the kinetics indicates that some ammonia slippage can be expected. However, as previously mentioned, the ammonia to NO_x conversion percentages found in the thermal oxidizers indicated a higher peak flame temperature than what was indicated by the combustion chamber temperature. The absence of any ammonia escaping from the thermal oxidizer is further evidence that the peak flame temperature was higher than the measured combustion chamber



7. Potential and actual NO_x from ammonia in SOGs as a function of gallons of condensate stripped



8. Conversion of NH_3 to NO_x for all combustion devices

temperature.

SUMMARY AND CONCLUSIONS

A number of kraft pulp mills currently steam strip foul condensates and burn the SOGs in thermal oxidizers, lime kilns or boilers to destroy odorous TRS compounds and volatile organics. Additional kraft mills are expected to install steam strippers to comply with the MACT portion of the Cluster Rule. To obtain permits to install and operate steam strippers, mills need to assess increases in emissions of pollutants such as SO_2 and NO_x associated with combustion of SOGs. To address concerns relative to NO_x, a study was conducted to determine the effect of SOG burning on NO_x emissions from thermal oxidizers, lime kilns, coal-fired boilers and combination wood-fired boilers at kraft pulp mills. At each of the seven mills in this study, the condensate stream sent to the steam stripper contained significant levels of ammonia. The ammonia content of stripper feed streams ranged from 94 mg/L to 508 mg/L, and the stripper feed flow rates were found to range from 160 gal/min to 515 gal/min. In all cases, the ammonia was entirely or almost entirely stripped from the stripper feed stream and became part of the SOGs sent to the combustion device. For the combustion units tested in this study, the NO_x emissions were found to range from 5 lb/hr to 46 lb/hr higher with SOG burning than they were without SOG burning.

From the above data, conversion of SOG ammonia to NO_x was calculated to range from 6.3% to 34.4% for the three thermal oxidizers, two coal-fired boilers, one combination wood/coal-fired boiler and two lime kilns tested in this study. The magnitude of the conversion apparently was not related to the type of combustion device.

In the range of normal operating conditions for the combustion units tested in this study, the conversion of ammonia to NO_x could not be specifically related to any of the process operating parameters. Limited data, however, suggest that for thermal oxidizers the conversion of ammonia to NO_x may decrease with combustion chamber temperatures below about 1500°F. For boilers, injecting the SOGs in the midst of the fuel injection area may reduce the conversion of ammonia to NO_x, possibly because most of the oxygen in this area may be consumed by the fuel before it can react with ammonia to form NO_x.

Testing at one boiler, one lime kiln and one thermal oxidizer indicated no emissions of unreacted ammonia. Apparently, the fraction of ammonia that was not oxidized to NO_x was reduced to molecular nitrogen. **TJ**

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Crawford

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INSIGHTS FROM THE AUTHORS

Q. *Why did you choose this topic to research?*
A. Kraft mills installing condensate steam strippers in response to the Cluster Rule needed to know how much NO_x emissions would result from burning the stripper off-gases.

Q. *How does this research either complement and support previous research you (or others) have done or how does it differ from previous research?*
A. Before this work was done, there were no comprehensive data available on the amount of NO_x emissions that could be expected from burning stripper off-gases in the various types of combustion devices used for that purpose (thermal oxidizers, lime kilns and power boilers).

Q. *What was the most difficult aspect of this research and how did you address that?*
A. The most difficult aspect of this work was determining the fraction of ammonia, from the stripper off-gases, that was oxidized to NO_x in the combustion devices. This problem was addressed by using a material balance around the steam stripper and combustion device.

Q. *What did you personally discover from this research? What was most interesting or surprising about your findings?*
A. There was no significant difference in the amount of ammonia to NO_x conversion between the different types of combustion devices. In addition, the amounts of ammonia to NO_x conversion were generally lower than one might have thought, based on the theoretical kinetics of the reactions of ammonia, nitric oxide and oxygen.

Q. *What's the next step?*
A. The next step is to determine the process factors that affect the amount of SOG ammonia converted to NO_x in the various combustion devices.

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We want to hear from you!

A feature we would like to include in this journal is "Letters to the Editor." To do that, of course, we need to hear from you.

Have you done research that supports or may question some of the findings reported in this issue? Do you have thoughts or concerns about the current direction or future of pulp and paper research? Do you have a question to pose to the readership? Do you have comments about the new *TAPPI JOURNAL*? If so, let us know.

To stimulate some discussion, we share this response to a reader survey sent to *TAPPI JOURNAL* subscribers this winter:

"If articles are applied, you cannot have peer review. Applied technologies are specific to a machine or process. What's the point of peer review?"

Comments?

You can submit your letters and comments to Don Meadows by email at dmeadows@tappi.org, by fax to +1 770 209-7400, or by surface mail to Don Meadows, Editor, TAPPI JOURNAL, 15 Technology Parkway S., Norcross, GA 30092, USA.