

Liquor-to-liquor differences in combustion and gasification processes: Nitrogen oxide formation tendency

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ABSTRACT

Seventeen black liquors are characterized for their combustion properties by studying the behavior of single liquor droplets or small liquor samples in laboratory furnaces under well controlled conditions. This paper discusses the NO formation tendency of the liquors that originated from North America, Scandinavia, and the Far East. Fourteen were kraft liquors, two were soda liquors, and one was a sulfite liquor. Most liquors used had nitrogen contents of 0.06%–0.20% dry solids. One liquor had 0.75% nitrogen. The authors measured the split between volatile nitrogen and char nitrogen, the tendency of the liquors to form NO during char combustion, and the total NO formation tendency of the liquors. The results showed differences among the liquors in their tendency to form NO in char combustion and black liquor droplet combustion. Total NO formation tendency test results showed good agreement with measured recovery boiler NO emission field data.

Application:

A procedure can successfully test for total NO formation tendency.

THIS IS THE SECOND PAPER IN A series of reports from an extensive study characterizing many black liquors for their combustion properties by novel methods developed at Åbo Akademi University (ÅAU) (1). The ÅAU methods study the behavior of single liquor droplets or small liquor samples in laboratory furnaces under well controlled conditions. This paper discusses the nitrogen oxide formation tendency for the various liquors.

In black liquor combustion, approximately two-thirds of the original nitrogen forms NH_3 and N_2 during devolatilization. Depending on the combustion conditions, the NH_3 can oxidize to NO and partly reduce to N_2 (2, 3). The nitrogen remaining in the char forms NO when subject to rapid oxidation. Under slow oxidation or gasifying conditions, the char nitrogen can remain in the smelt residue. Nitrogen in the smelt residue will almost quantitatively form NO when in contact with oxygen. The nitrogen can be removed with the smelt from the recovery furnace into the dissolving tank if the smelt is not exposed to oxygen. **Figure 1** shows NO formation routes in black liquor combustion and gasification (4).

Field measurements show that nitrogen oxide, NO_x concentration levels in the flue gases from black liquor recovery boilers typically are 60–135 ppm (5–9). The NO emissions originate almost exclusively in the fuel nitrogen (10–14).

This work compared 17 different liquors for their tendency to form NO. The first factor studied the split between volatile nitrogen and char nitrogen for all liquors. Next, we studied the tendency for the liquors to form NO during char combustion. We finally developed a test for total NO formation tendency of the liquors. This is the tendency of the liquors to form NO during devolatilization and char combustion. Recording the NO formation during the entire combustion process of single black liquor droplets measured the total NO formation tendency for the liquors.

BLACK LIQUOR STUDIED

This work studied 17 black liquors: 14 kraft liquors, two soda liquors, and one sulfite liquor. **Table I** provides a brief description and the chemical analysis of each liquor.

Nine kraft liquors were Scandinavian, and five were North American. The soda liquors were from North America and the Far East. The sulfite liquor was Scandinavian. Ten kraft liquors came from softwood pulping processes. Three came from hardwood or mixed hardwood processes, and one used eucalyptus. The two soda liquors originated from the pulping of straw and bagasse, and the sulfite liquor came from hardwood pulping. Liquor selection came from a bank of more than 40 black liquors. Each liquor complies with a strict set of collection and storage conditions. Each has also been characterized by conventional methods including elemental analysis and determination of

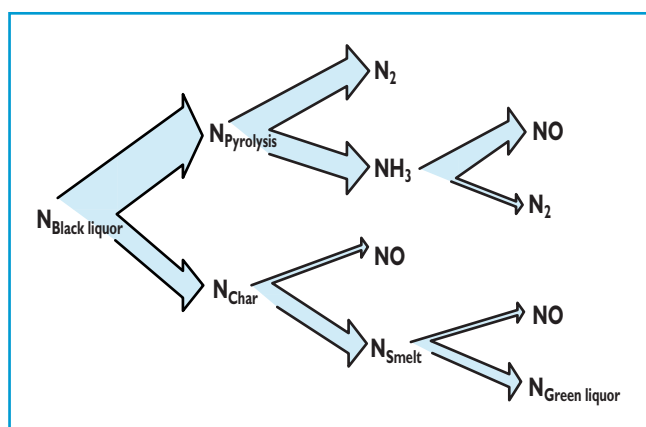
various physical properties such as dry solids, viscosity, etc. The liquors have undergone a thorough study of their combustion properties such as swelling during combustion, duration of char burning, and char reactivity by the ÅAU combustion characterization methods (1). Future papers will give details regarding establishment and maintenance of the liquor bank.

Three different methods analyzed the liquors for nitrogen. The Kjeldahl method was most suitable for measuring black liquor nitrogen contents (4). Nitrogen content of most liquors was 0.06%–0.20% of dry solids. The soda straw liquor had

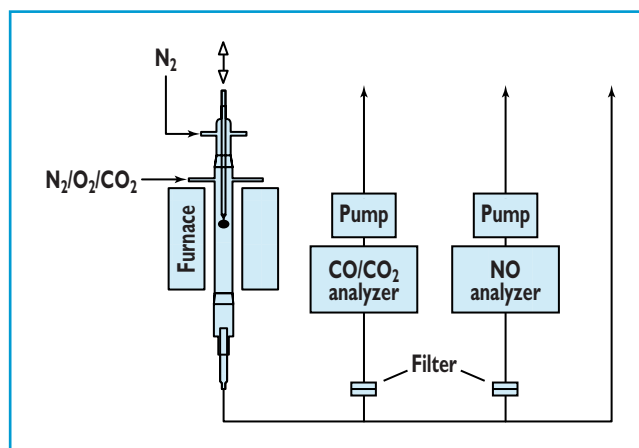
Liquor number	Liquor description	C, %	H, %	N*, %	Na, %	K, %	S, %	Cl, %
1	Kraft, softwood, Scandinavia	35.8	3.6	0.06	19.6	1.8	4.6	0.5
2	Kraft, hardwood, Scandinavia	33.1	3.4	0.07	20.8	1.8	5.0	0.6
4	Kraft, softwood, Scandinavia	34.4	3.3	0.06	22.8	1.6	3.7	0.5
5	Kraft, softwood, Scandinavia	33.9	3.3	0.07	19.6	3.2	5.7	0.3
6	Kraft, softwood, Scandinavia	34.6	3.4	0.07	17.2	3.2	5.4	0.3
7	Kraft, softwood, Scandinavia	34.1	3.4	0.07	19.9	1.2	5.5	0.2
8	Kraft, softwood, Scandinavia	34.2	3.4	0.07	19.7	1.2	5.1	0.2
9	Kraft, softwood, Scandinavia	34.6	3.3	0.07	19.8	1.4	5.2	0.5
10	Kraft, hardwood, Scandinavia	33.2	3.3	0.08	20.8	2.6	5.2	0.3
11	Kraft, eucalyptus, North America	37.3	3.6	0.09	17.3	1.8	3.4	1.6
12	Kraft, softwood, North America	34.3	3.4	0.06	19.0	3.0	5.2	0.9
13	Kraft, softwood, North America	36.8	3.7	0.08	18.7	1.3	4.4	0.6
14	Soda, bagasse, North America	34.0	3.7	0.19	18.9	0.6	1.3	0.5
15	Soda, straw, Far East	35.4	3.8	0.75	15.8	1.9	1.6	3.6
19	Kraft, mixed hardwood, North America	35.0	3.5	0.11	16.7	3.1	4.0	0.4
20	Kraft, softwood, North America	38.0	3.7	0.09	18.6	1.0	3.6	1.7
23	Sulfite, hardwood, Scandinavia	33.5	4.0	0.2	14.2	1.1	7.6	0.4

*Kjeldahl nitrogen

1. Black liquors examined



1. Fuel nitrogen conversion pathways (4)



2. Experimental equipment

a much higher nitrogen content of 0.75% of dry solids. Nitrogen contents of the four hardwood liquors were slightly higher than those of the ten softwoods. The bagasse-based sulfate liquor had a nitrogen content of 0.19%, and the ammonium-based liquor had a nitrogen content of 0.20%.

The black liquors and the code numbers used in this work are the same as those in earlier work (1, 4).

EXPERIMENTAL

Figure 2 shows the experimental apparatus used in this study. It consisted of a reactor, an NO analyzer, a

CO and CO₂ analyzer, a gas sampling pump, and a computer for data collection. A predetermined gas mixture flow passed through a 2.6 cm inner diameter quartz reactor inside the tube furnace. From the outlet of the quartz reactor, a sample of the gases was pumped continuously to two different analyzers: an NO analyzer (chemiluminescence) and a one cell CO and CO₂ analyzer [nondispersive infrared (NDIR)]. A computer recorded the output signals.

For each experiment, a single droplet of black liquor was placed on a quartz sinter inserted in the

down-flowing gas stream on the end of a long quartz glass rod. The sinter was in the down position 0.05 m above the center of the furnace about 0.4 m below the point of introduction. After the experiment, the sinter disc with the residue was lifted to a nitrogen quench located about 0.15 m above the heated zone of the reactor. After cooling in the quench zone, the residue was removed. The recorded curves of NO, CO, and CO₂ concentration vs. time were integrated. The total amount of nitrogen as milligrams of nitrogen per 100 g of black liquor

solids, mg N/100 g BLS, was reported. The CO₂ curve indicated the progress of the char combustion.

Three types of experiments were performed:

- Analysis of nitrogen remaining in char after devolatilization
- Measurement of NO formation during char combustion
- Measurement of NO formation during combustion of single black liquor droplets.

For measurement of nitrogen remaining in char, the droplets were devolatilized at 800°C for 100 s in a nitrogen flow. The char was removed after cooling, weighed, and analyzed for nitrogen at an independent laboratory. When measuring the formation of NO during char combustion, the black liquor droplets were devolatilized as in the previous experiments. Then the gas flow to the reactor was switched to a 2.5% O₂ mixture. The furnace temperature was 700°C. The measurements of NO formation during combustion of single black liquor droplets were performed at 900°C in 10% O₂.

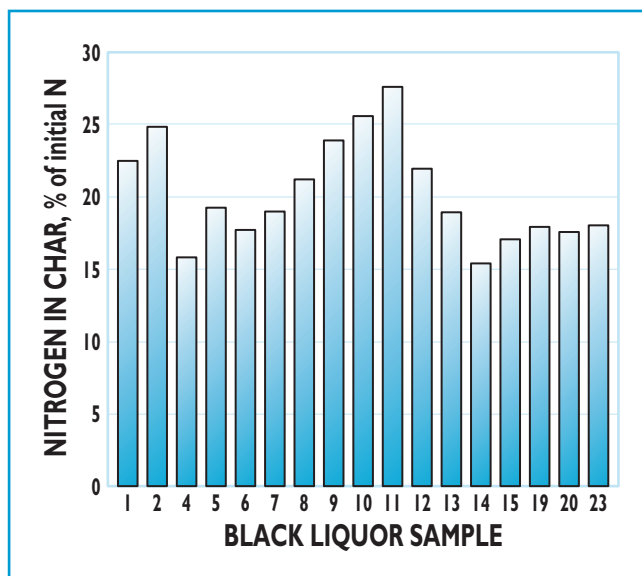
For practical reasons, the initial mass of droplets used in the tests was 35–45 mg initial mass (wet basis). This corresponds to an initial droplet diameter of 3–4 mm.

RESULTS AND DISCUSSION

Char nitrogen yield for liquors

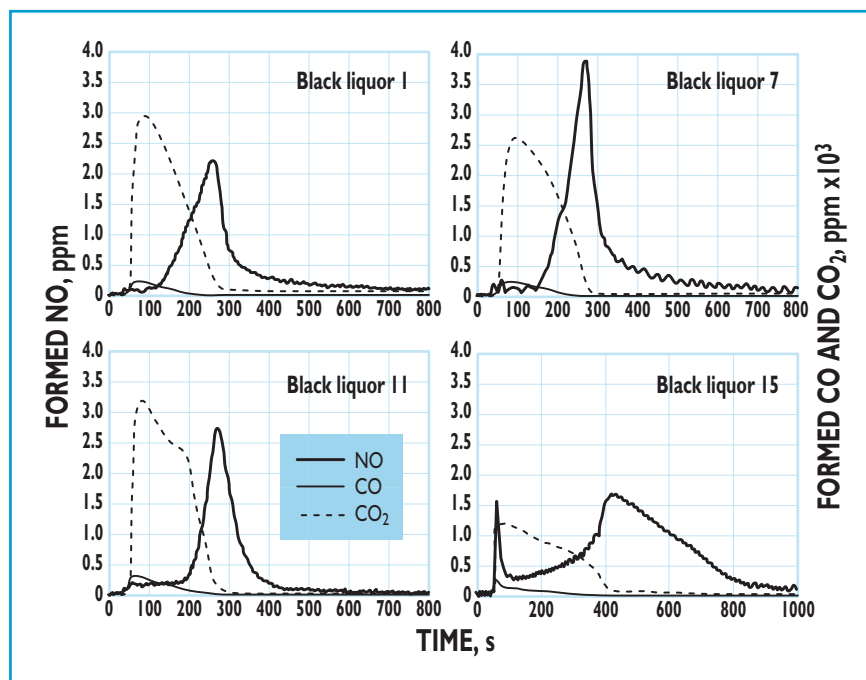
To determine the split of liquor nitrogen into volatile nitrogen and char nitrogen, we devolatilized single black liquor droplets for 100 s in N₂ at 800°C and analyzed the remaining char for nitrogen. All chars from the 17 black liquors were analyzed using the high temperature combustion (HTC) method (4).

Figure 3 shows the nitrogen remaining in char, “char nitrogen yield,” as a percentage of initial nitrogen in the black liquor. The results show that the char nitrogen yield for most of the liquors is 15%–20%. Liquors 4 and 14 have the lowest char nitrogen yield at 15%. Liquor 11 has the highest char nitrogen yield at 26%. For liquors 14, 15, and 23, that had the highest nitrogen contents, the char nitrogen yield values are 9–128 mg N/100 g BLS for 100 grams original black liquor solids.

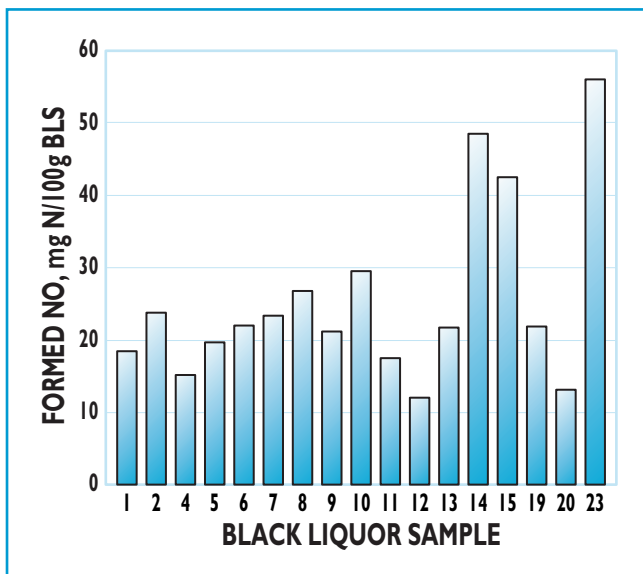


3. Nitrogen remaining in char after devolatilization in N₂ at 800°C for 100 s

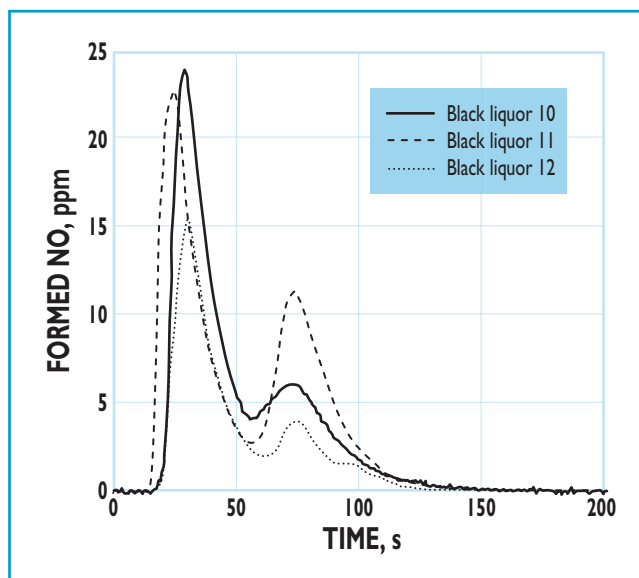
These values are lower than those reported elsewhere (15) that showed char nitrogen yields of approximately 50%. Those measurements used a laminar entrained flow reactor using small predried black liquor particles (< 125 µm). The heating rate in that test is consequently much higher than the heating rate in our experimental system. In our study, the particle size is near the real particle size in recovery furnaces. Our data may therefore be more directly applicable to recovery boiler conditions.



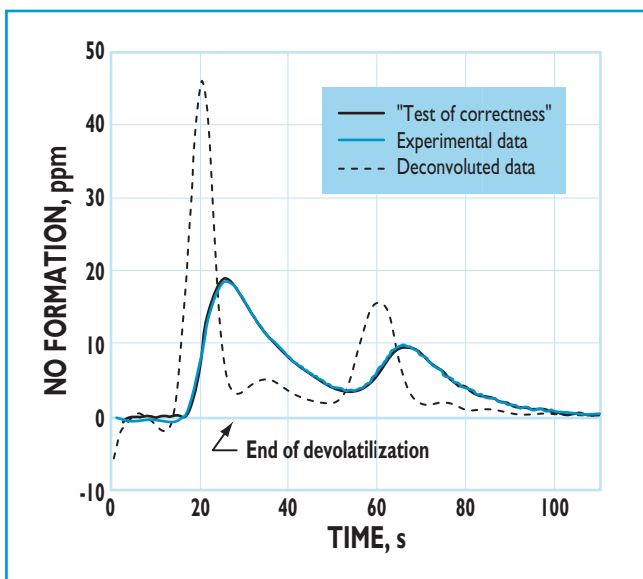
4. Formation of NO, CO, and CO₂ during char combustion of black liquor char in 2.5% O₂ at 700°C for black liquors 1, 7, 11, and 15



5. Total NO formed during char combustion in 2.5% O₂ at 700°C for all liquors tested



6. Typical NO formation curves for the combustion of single black liquor droplets in 10% O₂ at 900°C for black liquors 10, 11, and 12



7. Typical result for processing the data for NO formation at combustion of single black liquor droplets in 10% O₂ at 900°C for black liquor 6

Char NO formation tendency

The formation of NO from the combustion of char from a set of different black liquors has not been previously studied. We wanted to compare the tendency for all 17 liquors to form NO during char oxidation. We measured the formed NO during char combustion at 700°C in 2.5% O₂.

Figure 4 shows typical NO, CO, and CO₂ formation curves for experiments on the char combustion of black liquors 1, 7, 11, and 15. The four liquors were chosen with no specific black liquor property in mind to give typical examples of NO formation. The NO formation for the remaining liquors showed very similar behavior.

All liquors have a similar char combustion curve for CO₂ formation. When oxygen is introduced into the reactor, a rapid increase to a maximum CO₂ formation occurs. After the maximum CO₂ formation, the oxidation rate starts to decrease, probably due to the gradual decrease in char particle surface area. The char combustion rate of liquor 15 is about one-third lower than for the other liquors.

Formation of NO during char combustion shows an interesting pattern. At the beginning of char combustion, the formation of NO is almost zero for liquors 1, 7, and 11. At the end, when CO₂ decreases, an increase in the NO formation occurs. After char combustion, a significant increase in the NO formation is observed. This NO formation finally declines, probably after consumption of all the nitrogen in the residue.

Black liquor 15, the soda straw liquor, shows a slightly different pattern. As noted above, its char combustion is slower than for the three other liquors. In addition, a distinct peak in the NO formation at the beginning of the experiment occurs. After this, the NO formation becomes rather slow. This peak could originate from secondary pyrolysis products released and oxidized when introducing O₂ into the reactor. Again, a rapid increase in NO formation at the end of char combustion occurs. Then the NO formation slowly decays until the nitrogen appears to be consumed during a time that is twice the char combustion time.

Forssén *et al.* (4) reported these findings earlier for char combustion using one black liquor at varying temperatures and oxygen contents. At fast oxidation of the char, NO formation was simultaneous with carbon release (CO₂ formation). With slow char oxidation, the

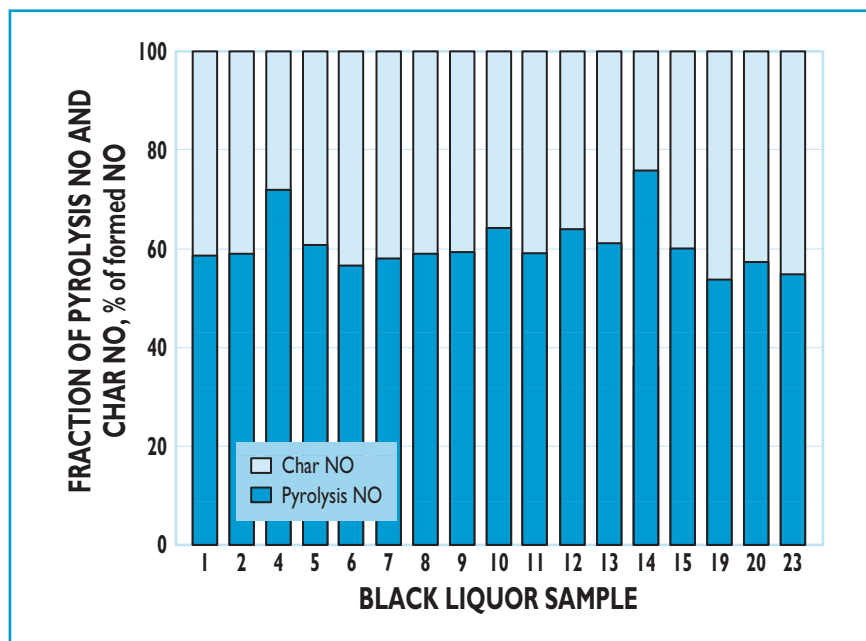
NO formation shifted to the end of the carbon release period. The nitrogen remained in the inorganic residue where it readily formed NO when further oxidized. **Figure 5** shows the total amount of NO formed during these experiments. The NO formation for most of the liquors is 10–25 mg N/100 g BLS. Liquor 12 had the lowest formation of NO. Liquors 14, 15, and 23 have the highest NO yields of about 50 mg N/100 g BLS. The NO formation values for liquors 14, 15, and 23 are underestimated because the NO formation was very slow and had not ended at the completion of the experiment.

The measurement of NO formation during char combustion and the analysis of nitrogen remaining in char showed discrepancies. The nitrogen found as NO during char combustion was lower than the amounts of nitrogen analyzed in the char only for liquors 11, 12, 15, and 20. The liquors that had a release of NO higher than the nitrogen found in char showed a clear trend of 5–10 mg N/100 g BLS higher than that corresponding to the nitrogen found in their char. Temperatures were not sufficiently high for formation of thermal NO.

The discrepancies can be due to the procedure of the analysis of nitrogen in the char (13). From the char combustion experiments in this study, we estimate the char nitrogen yield to be 20%–30% of the initial nitrogen in the black liquors. Additional analyses of char nitrogen using different methods are underway.

Total NO formation tendency

The total tendency to form NO was measured by recording the NO formation during combustion of single black liquor droplets in 10% O₂ at 900°C. **Figure 6** shows typical NO formation curves for black liquors number 10, 11, and 12. The CO₂ and CO formations were not measured in these experiments.



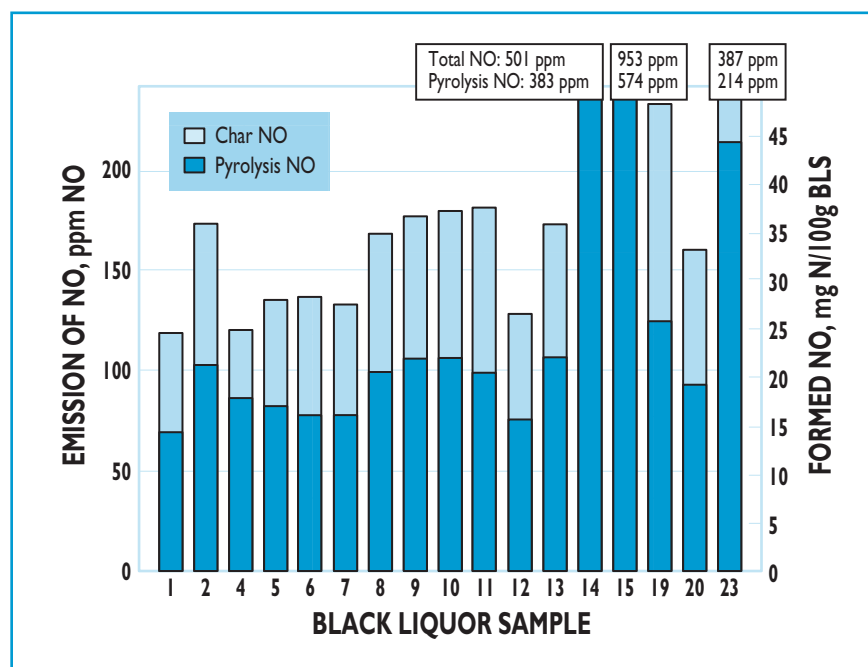
8. Percentage of pyrolysis NO and char NO formed during the combustion of single black liquor droplets in 10% O₂ at 900°C

The NO formation curves show two separate peaks. The first peak is a result of the oxidation of the nitrogen species in the released pyrolysis gases. After the devolatilization, the NO formation decreases and reaches a minimum at approximately 50 s from the start of the experiment. At this stage, an increase in the NO formation occurs that reaches a peak at approximately 75 s. The second peak originates from the end of char combustion. Finally, the NO formation ends at approximately 100 s. The NO formation for the remainder of the liquors showed similar behavior.

The measured response at the analyzer is a result of the NO formed during combustion and the dispersion of the formed NO when the gases pass through the reactor and the tubing to the analyzer. This results in a dispersion of the NO concentration measured at the analyzer (16). Processing the experimental data can estimate the effect of the dispersion. In the processing, the dispersion of a tracer in the reactor is measured followed by a so-called deconvolution on the experimental data using the measured tracer dispersion data. The deconvoluted signal obtained includes noise that is finally filtered.

The result is an estimation of the real NO formation process for the droplet. Liliendahl *et al.* (17) processed data when measuring true devolatilization rates for devolatilization experiments of coal particles and developed a data processing routine using commercially available software. We have modified their routines to a form suitable for use in this work. **Figure 7** shows a typical result for a signal processing calculation. The figure includes the measured NO formation signal, the deconvoluted signal, and the “test of correctness” signal calculated from the deconvoluted signal. The “test of correctness” signal is barely visible behind the experimental data. The “test of correctness” curve showed that the NO formation calculated from the processed signals agreed with the NO formation calculated from the experimental data for all runs.

The processed data shows that the NO formation curves consist of two clearly separated peaks. Both peaks are much higher and shorter in the processed form than in the original data. The strong second peak agrees with the finding that NO also forms at the end or after the char combustion.



9. Estimated NO emissions from a recovery boiler during the liquors studied in this work

We have divided the total NO formed during the experiments into "pyrolysis NO" and "char NO." Pyrolysis NO is the amount of NO in the first peak of the processed curve. Char NO is the amount of NO formed after the first peak in the processed curve. Figure 7 shows the point we have chosen for the end of devolatilization in this experiment. Figure 8 shows the split between pyrolysis NO and char NO. For most liquors, almost 60% of the total NO is pyrolysis NO. Liquors 4 and 14 have a larger proportion of pyrolysis NO at approximately 70% of the formed NO. Liquor 19 has the smallest fraction of pyrolysis NO at 55% of formed NO.

Integrating the area under the NO formation curves provides the total amount of NO formed during the combustion experiments. The total NO formed in Fig. 9 (right y-axis) in measuring the total NO formation tendency is 25–200 mg N/100 g BLS. Liquor 15 has the highest NO formation, and liquors 1 and 4 have the lowest NO formation. On average, about 45% of the black liquor nitrogen forms NO in these experiments.

We also converted the measured total NO formation tendency results to corresponding recovery boiler NO emissions. Figure 9 (left y-axis) shows the calculated emission levels reported as NO concentration in ppm for the dry flue gases with 8% O₂. The emissions are split into pyrolysis NO and char NO.

For liquors with nitrogen content of 0.06%–0.11%, the emission levels converted using only the values for measured pyrolysis NO are 70–120 ppm. This agrees well with field measurements of NO emissions for recovery boilers. When considering both pyrolysis NO and char NO, the emission levels increase to 120–180 ppm. Liquors 14, 15, and 23 show much higher levels of NO emissions. Using only the pyrolysis NO gives emissions higher than 210 ppm. With the char NO added, the emission level rises to more than 380 ppm.

CONCLUSIONS

We successfully measured the NO formation tendency for 17 liquors using three different experimental procedures. The nitrogen content of most liquors was 0.06%–0.20% of BLS. One liquor (soda straw) contained 0.75% N in BLS. The nitrogen

contents of the hardwood liquors were slightly higher than the softwood liquors. The bagasse-based soda liquor and the ammonium-based sulfite liquor had nitrogen contents of 0.19% and 0.20%, respectively.

Char nitrogen analysis showed that 15%–20% of black liquor nitrogen remains in the char during devolatilization. Measurements of the NO formation tendency of the black liquors during char combustion indicate 5%–10% higher levels of nitrogen in char. For the liquors studied, no major differences occurred in the NO formation pattern during char combustion. The total amounts of NO formed were 20%–35% of the original nitrogen for all liquors. The ranking of the liquors for the amount of nitrogen found in char and the ranking for the amount of NO formed during char combustion agreed with each other.

Total NO formation tendency for the liquors was measured by recording the NO formation during the entire combustion process of single black liquor droplets. The results showed that the developed procedure for measuring the total NO formation tendency was successful. The NO formation during combustion of single black liquor droplets was split into pyrolysis NO and char NO. About 60% of the NO originates from the devolatilization stage. When converted to recovery boiler NO emissions, the measurements showed good agreement with typical recovery furnace field data. The total NO formation tendency test indicates a minimum and a maximum level for recovery boiler NO emission levels that originate from the fuel nitrogen. **TJ**

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LITERATURE CITED

1. Whitty, K., Backman, R., Forssén, M., et al., *J. Pulp Paper Sci.* 23(3):119(1997).
2. Aho, K., Nikkanen, S., and Hupa, M., *Tappi J.* 77(8):182(1994).
3. Aho, K., Vakkilainen, E., and Hupa, M., *Tappi J.* 77(5):121(1994).
4. Forssén, M., Hupa, M., Pettersson, R., et al., *J. Pulp Paper Sci.* 23(9):439(1997).
5. Jones, A. K. and Stewart, R. I., *TAPPI 1992 International Chemical Recovery Conference Proceedings*, TAPPI PRESS, Atlanta, p. 365.
6. La Fond, J. F., Jansen, J. H., and Eide, P., *Tappi J.* 77(12):75(1994).
7. Osborne, D. M., *Tappi J.* 75(5):107(1992).
8. Shuey, B., Strandell, O., Kaila, J., et al., 1995 *International Chemical Recovery Conference Proceedings*, CPPA, Montreal, p. B5.
9. Hyöty, P. and Mäntyniemi, J., *TAPPI 1992 International Chemical Recovery Conference Proceedings*, TAPPI PRESS, Atlanta, p. 405.
10. Nichols, K. M. and Lien, J. L., *Tappi J.* 76(3):185(1993).
11. Nichols, K. M., Thompson, L., and Empie, H. J., *Tappi J.* 76(1):119(1993).
12. Veverka, P. J., Nichols, K. M., Horton, R. R., et al., *TAPPI 1993 Environmental Conference Proceedings*, TAPPI PRESS, Atlanta, p. 777.
13. Martin, D. M., Malcolm, E. W., and Hupa, M., *Chemical and Physical Processes in Combustion*, The Combustion Institute, Pittsburgh, 1994, p. 294.
14. Adams, T. N., Stewart, R. I., and Jones, A. K., *TAPPI 1993 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 625.
15. Iisa, K., Carangal, A., Scott, A., et al., *International Chemical Recovery Conference Proceedings*, CPPA, Montreal, 1995, p. B241.
16. Levenspiel, O., *The Chemical Reactor Omnibook*, Oregon State University, Corvallis, 1989, p. 61.2.
17. Liliendahl, T., Sjöström, K., and Wiktorsson, L.-P., *AIChE J.* 37(9):1415(1991).