Fate of biosludge nitrogen in black liquor evaporation and combustion

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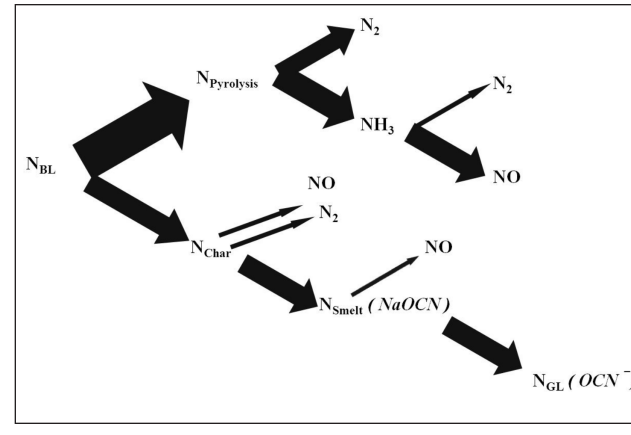
ABSTRACT: At many mills, biosludge, which has a high nitrogen content, is added to black liquor and burned in kraft recovery boilers. The aim of this work was to determine the fate of biosludge nitrogen in the high solids black liquor concentrators and in the recovery boiler. Specifically, does biosludge addition result in higher nitric oxide (NO) and cyanate formation during black liquor combustion? To obtain this information, samples were collected from the chemical recovery cycle of a Finnish kraft pulp mill along with relevant process data. Laboratory combustion experiments clearly showed an increase in NO formation for the mill black liquor with biosludge, but no clear increase in nitrogen oxide emissions was detected in the recovery boiler after biosludge addition. Analysis of the green liquor samples from the dissolving tank showed a significant increase in nitrogen exiting the recovery boiler as cyanate. This finding was supported by laboratory tests studying cyanate formation. The increased cyanate results in increased ammonia formation in the recausticizing cycle, which can lead to higher NO emissions, as seen in the noncondensible gas incinerator at the mill.

Application: This work identifies the fate of biosludge nitrogen in black liquor evaporation and combustion when biosludge is added to black liquor in the second effect of a seven-effect evaporator set.

Nitrogen oxide (NO_x) emissions in recovery boiler furnaces originate primarily from black liquor nitrogen (fuel nitrogen). Because of the relatively low furnace temperature, thermal and prompt NO_x are minor sources of the NO_x emissions in kraft recovery boilers [1-3]. The nitrogen in black liquor originates from the wood and white liquor used in kraft pulping [4]. Wood contains 0.05-0.25 wt-% nitrogen, depending on the wood species and environmental factors [5]. After cooking, nitrogen exits the digester mainly with the weak black liquor (~87%) and with the blow gases (~13%) [6]. Between 10% and 20% of the nitrogen in weak black liquor is volatilized in the early evaporation stages as ammonia (NH_3) or other volatile nitrogen compounds ending up in methanol (MeOH) and noncondensible gas (NCG) [4,6].

Figure 1 shows the different pathways for nitrogen entering the recovery boiler with black liquor [7]. Roughly 60%-70% of the nitrogen in as-fired black liquor is released during devolatilization, mainly as nitrogen (N_2) and ammonia (NH_3). Ammonia is further oxidized to nitric oxide (NO) or reduced to N_2 [7-10]. The rest of the nitrogen remains in the char. A small portion of the char nitrogen is converted to NO or N_2, and the rest remains in the smelt as cyanate (OCN^-). A portion of the smelt nitrogen is oxidized or thermally decomposed in the lower furnace, but about 20%-30% of the as-fired black liquor nitrogen will exit the recovery boiler with the smelt and be found in the green liquor [6,11,12].

The exact mechanisms behind cyanate formation in black liquor combustion are unknown [13]. Previous studies show that black liquor promotes cyanate formation when a high nitrogen content fuel is mixed with black liquor [14]. This suggests that cyanate formation might be related to the catalytic char gasification reactions. Smelt from the recovery boiler is mixed with water in the smelt dissolver to form green liquor. The cyanate in green liquor decomposes to form NH_3, which can increase the overall emissions of kraft pulp mills [13,15,16].



1. Path of nitrogen in black liquor combustion.

The overall distribution of the combustion products of black liquor nitrogen can be roughly divided into nearly equal fractions of N_2, NO_x, and OCN^- [17,18]. This ratio of NO_x, N_2, and smelt nitrogen from the recovery boiler combustion can be altered by adjusting the firing conditions [19,20] and low NO_x and low OCN^- can be obtained simultaneously [19].

Kymäläinen et al. determined the effects of different process variables on the fate of nitrogen in the chemical recovery cycle, including biosludge addition [21]. Biosludge consists of dead bacteria from biological waste water treatment and sludge from the mechanical clarification of waste water [22].

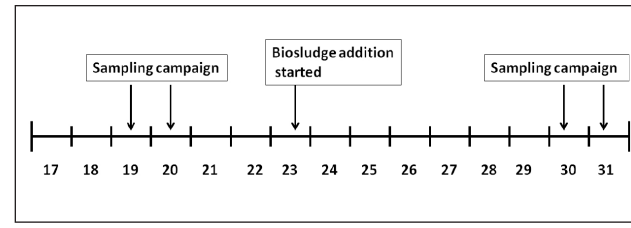
Biosludge in pulp mills can be disposed of by burning, either by mixing it with bark or with black liquor before combustion. At one mill, biosludge addition to black liquor increased the nitrogen content of the as-fired black liquor by about 30% [21]. No increase was seen with the addition of biosludge at a second mill, which did not have a clear period of consistent biosludge addition during the sampling campaign [21]. Because the mill in our study went from a long period of no biosludge addition to a long period of biosludge addition, we were able to draw clear conclusions about the fate of biosludge nitrogen.

The objective of this work was to get a clearer picture of the fate of the biosludge nitrogen in the evaporation and combustion of black liquor with biosludge added. Biosludge is co-combusted at several mills without any clear increase in NOx emissions [21]. Our study was conducted to better understand the fate of biosludge nitrogen and the potential effect on the overall nitrogen emissions from the kraft chemical process [21]. This was achieved by collecting and analyzing mill samples and through laboratory experiments. The variables studied in this work included 1) the nitrogen content of the black liquor and biosludge samples from different effects in the evaporation train; 2) NO_x emissions at the recovery boiler, at the lime kiln, and at the NGC boiler; 3) NO formation in laboratory conditions; and 4) the cyanate content in mill green liquor samples and laboratory-made smelts. The effect of biosludge addition on black liquor combustion characteristics (i.e., combustion times and swelling) also was obtained from the laboratory combustion tests.

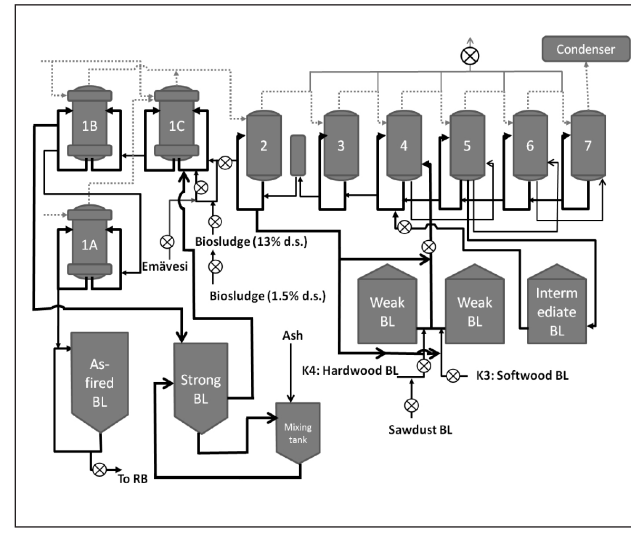
EXPERIMENTAL

The samples for this work were acquired from a Finnish pulp mill in May 2011. The nitrogen concentrations from black liquor samples taken from the same mill in December 2010 are included for comparison. The pulp mill has three digesters: one for softwood pulping, one for hardwood pulping, and one for sawdust pulping. The black liquor from the three digesters are mixed and concentrated to greater than 80% dry solids in a seven-effect evaporator set. The high-volume, low-concentration gases from the tanks in pulping and evaporation are burned in the recovery boiler, and the high-volume, low concentration NCG from the tanks in recausticizing are burned in the lime kiln. The methanol and NCG from the stripper are burned in a separate NCG boiler. Biosludge from the waste water treatment is burned during winters in the bark boilers. During summers, the bark boiler is shut down and biosludge is mixed with black liquor and burned in the recovery boiler. The sampling campaign in May 2011 was conducted to obtain mill samples with and without biosludge addition to the black liquor (**Fig. 2**).

Black liquor samples were collected from different stages of black liquor evaporation (**Fig. 3**), and green liquor samples were taken from the smelt dissolver. During the period when biosludge was added to the black liquor, biosludge samples before and after mechanical drying also were collected. The biosludge had an initial dry solids content of 1.5% and was



2. Dates of sampling campaigns in May 2011.



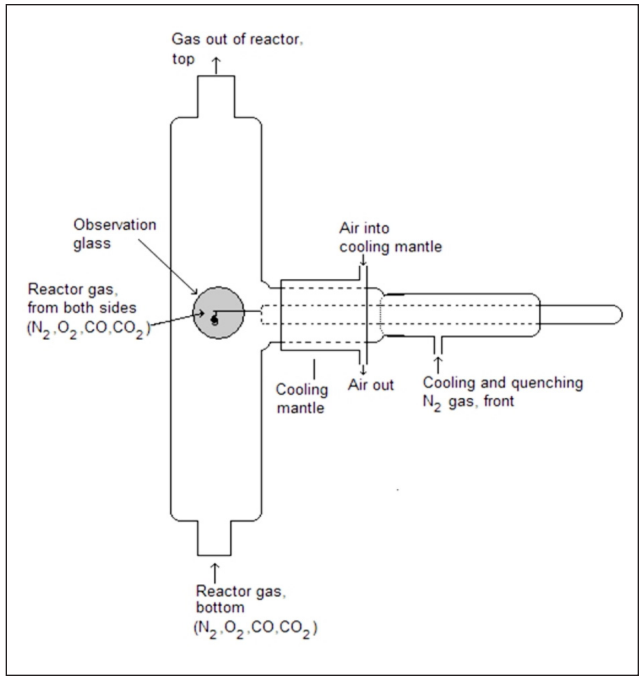
3. Sampling points at the pulp mill.

mechanically dewatered to approximately 13% dry solids before being mixed with the black liquor from the second effect evaporator. During the period when biosludge was added, the amount of added biosludge to black liquor was 0.5-1.2 wt-% on a dry solids basis. The biosludge flow to the second effect evaporator was almost constant to ensure efficient disposal of formed biosludge. The flow and dry solids of black liquor in the evaporation varied during the sampling campaign.

Morning and afternoon samples were pulled on each of the four sampling days, resulting in a total of eight as-fired black liquor samples and eight green liquor samples being collected during the campaign days in May. Thus, four of these samples were collected during a period when no biosludge was added and four when biosludge was added to black liquor. Additionally, process data from evaporation, the recovery boiler, the lime kiln, and the NCG boiler were obtained from the pulp mill. All NO_x emissions are from on-line measurements at the mill.

The total nitrogen content of selected black liquor and biosludge samples were analyzed with a modified Kjeldahl method using Devarda's alloy (CAS No. 8049-11-4), based on the SFS 5505 standard method. Cyanate was analyzed in laboratory-prepared smelts and in the mill green liquors with ion chromatography with a 1.3 mM sodium carbonate (Na_2CO_3) and 2.0 mM sodium bicarbonate ($NaHCO_3$) solution as eluent, using an anion column for separation, and a conductivity detector for quantifying the cyanate anions [23].

Combustion and cyanate formation experiments were con-



4. Schematic drawing of the quartz glass reactor used in the combustion experiments [24].

ducted for the collected as-fired black liquor samples at Åbo Akademi University in a quartz glass reactor (**Fig. 4**). Six 10 ±0.5 mg droplets of each as-fired black liquor sample collected were burned at 1100°C and 3% O_2 in N_2. The formed NO was measured with an on-line chemiluminescence analyzer and the formed CO and CO_2 were measured using an infrared analyzer. The combustion of the droplets was recorded with a video camera to determine swelling and combustion times.

The combustion of black liquor droplets can be divided into four stages: drying, devolatilization, char burning, and smelt coalescence [25]. The combustion times for the different stages were determined from the recorded video. Because of the high furnace temperature, we could not determine the drying time. Devolatilization time is defined as the time from the appearance of the flame to the disappearance of the flame. Char burning time is defined as the time from the point where the visible flame disappears to the point where smelt coalescence occurs [14].

The maximum swollen volume of the droplet was estimated by capturing an image from the recorded video. The captured image was compared to a circle or an ellipse with the same area. Based on the area, we calculated the volume of a corresponding sphere or ellipsoid. The maximum swollen volume is represented as cm^3/g of dry black liquor.

Cyanate formation in the collected as-fired black liquors was determined by pyrolyzing six droplets (14 ±1 mg) of each as-fired black liquor at 800°C in 100% N_2 for 10 s to form chars. The chars were then gasified at 800°C in 13% CO_2/87% N_2 to obtain the smelt. The smelts were dissolved in ultrapure water and analyzed for cyanate. The water to smelt ratio was 0.7 mL of ultrapure water per 1 mg of smelt.

RESULTS AND DISCUSSION

We have divided our results and discussion into two sections. The first section focuses on the fate of biosludge nitrogen, and the second part focuses on the combustion characteristics (i.e., combustion times and swelling) of the as-fired black liquors with and without biosludge addition.

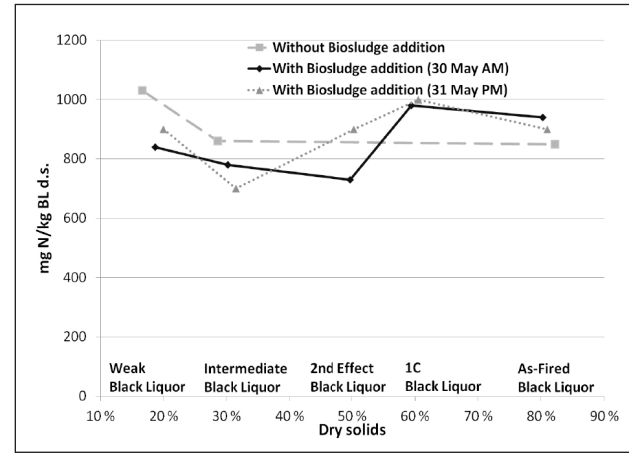
Fate of biosludge nitrogen

Table I shows the nitrogen content of the analyzed as-fired black liquors. The first four as-fired black liquor samples were pulled during the period before biosludge addition was made to the black liquor, and the last four as-fired black liquors were pulled about a week after biosludge was first added to the black liquor.

Figure 5 shows how the nitrogen concentration of black liquor changed during different stages of evaporation. The dashed line in Fig. 5 shows the nitrogen content of different dry solids black liquor from December 2010. No biosludge was added at that time. The solid line and dotted line are for the black liquor when biosludge was added after the second effect. Samples from May 30 and 31 were analyzed. Figure 5 shows that roughly 20% of the total nitrogen was removed in the early stages of evaporation because of the release of vola-

Black Liquor Sample		Kjeldahl-N (wt-% d.s.) As-Fired Black Liquor
19 May	AM	0.069
	PM	0.069
20 May	AM	0.066
	PM	0.068
30 May	AM	0.094
	PM	0.088
31 May	AM	0.090
	PM	0.092

I. Nitrogen content of analyzed as-fired black liquors.

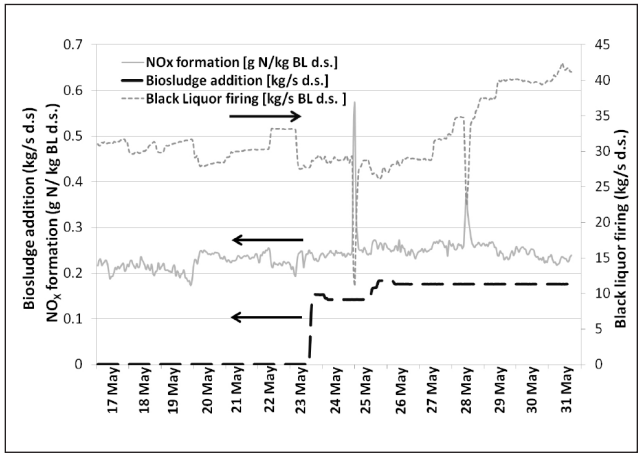


5. Nitrogen concentration (mg N/kg dry black liquor) of different dry solids black liquor.

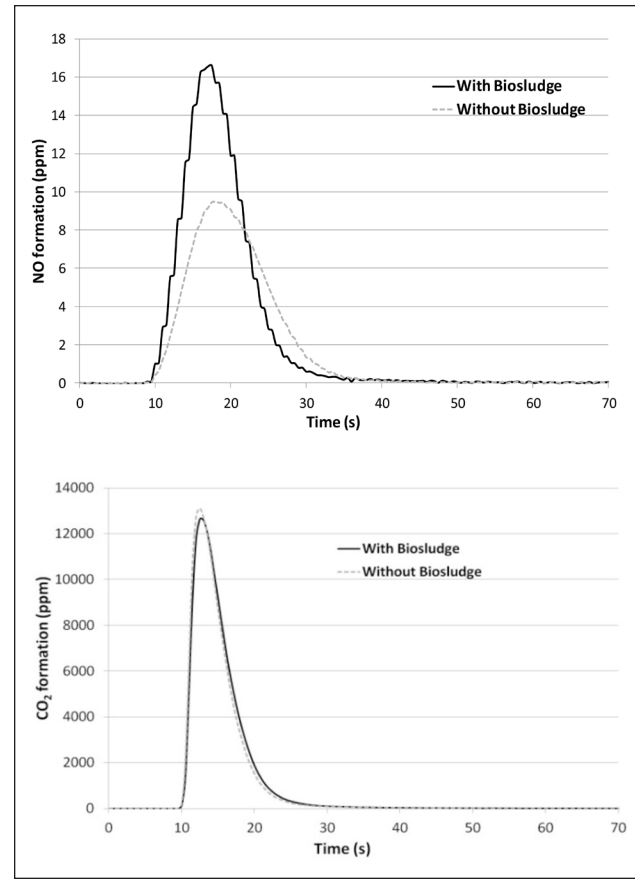
tile species (i.e., NH_3 and low molecular weight organic compounds), which is consistent with previously published studies [4,6]. For the black liquor without biosludge addition, the nitrogen content remained constant after the early stages of evaporation, indicating that the remaining nitrogen was stable. The added biosludge had a nitrogen content of 5.3 wt-% dry solids basis and an NH_3 content of 0.3 wt-% N on a dry solids basis. The NH_3 is expected to be volatilized in the concentrators. It was not clear before this study whether additional nitrogen would be volatilized from the biosludge. Based on the black liquor analysis, no significant release occurred. The samples collected on the afternoon of May 31 show that the nitrogen content of the black liquor increased before biosludge addition, but the reason for the increase in nitrogen content remains unknown. Biosludge addition results in an increase in the nitrogen content of about 25% with the NH_3 and perhaps some lower molecular weight nitrogen containing organics was released in the black liquor concentrators.

Figure 6 shows the NO_x emissions as g N/kg black liquor dry solids and biosludge addition as kg/s dry solids on the primary y-axis during a 15-day period. In Fig. 6, the secondary y-axis shows the black liquor firing as kg dry solids/s. Biosludge addition to the black liquor was started on May 23. Although the biosludge increased the nitrogen content of the as-fired black liquor, no clear increase in NO_x emissions in the recovery boiler was detected. The spikes in the NO_x emissions correspond to sudden drops in the black liquor firing rate.

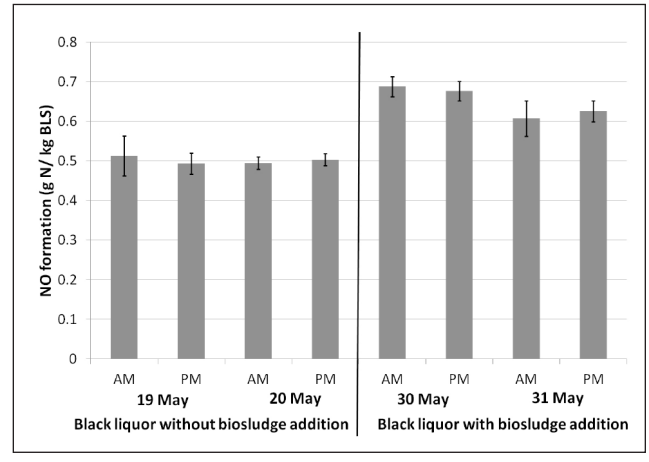
No clear increase in the NO_x emissions could be detected at the recovery boiler when biosludge was added to black liquor, but combustion experiments conducted in the single particle reactor showed a clear increase in NO formation with biosludge addition (**Figs. 7** and **8**). Figure 7 shows the average NO and CO_2 evolution in ppm (mole fraction) of the as-fired black liquors when incinerated in the laboratory single particle reactor. CO_2 evolution differed little between the two black liquors, but the NO evolution is clearly higher for the black liquor with biosludge addition, particularly during devolatilization.



6. NO_x emissions, black liquor firing rate, and biosludge addition during a 15-day period.

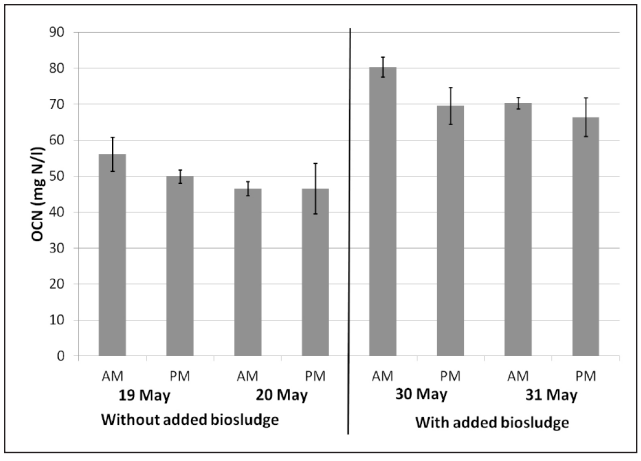


7. NO (top) and CO_2 evolution (bottom) in ppm of the as-fired black liquors with and without biosludge addition at 1100°C and 3.3% O_2.

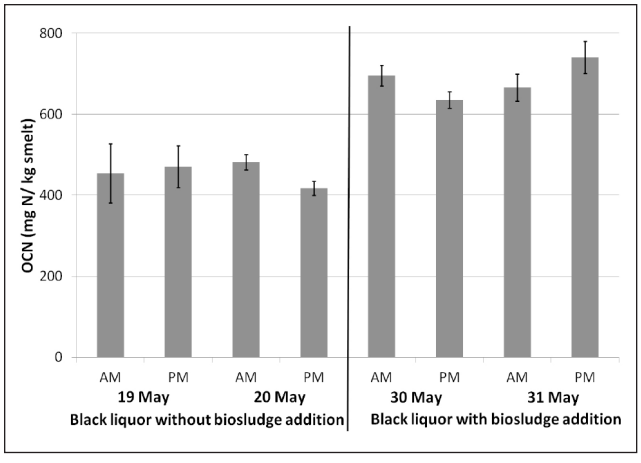


8. Average NO formation of as-fired black liquor samples at 1100°C and 3.3% O_2. Error bars represent 1 standard deviation for six replicate combustion tests.

Figure 8 shows NO formation (g N/kg black liquor solids) for the individual as-fired black liquors. Droplet combustion tests for the liquors with biosludge addition clearly show an increase in NO formation as a result of the high nitrogen content in biosludge. In the droplet combustion tests, the smelt nitrogen also reacts, whereas in a recovery boiler, about 20%-



9. Cyanate content of the mill green liquors. Error bars represent 1 standard deviation for six replicate analyses.

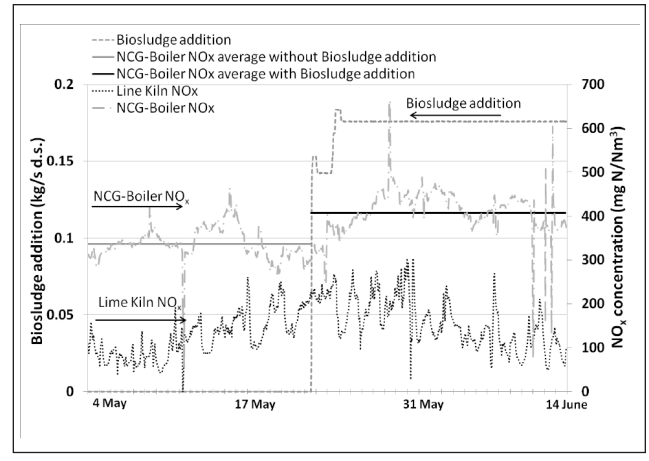


10. Cyanate formation after pyrolysis and gasification to 100% smelt for the as-fired black liquor samples. Error bars represent 1 standard deviation for six replicate experiments.

30% of the nitrogen in black liquor exits with the smelt. This could at least partially explain the increase in NO formation seen in the single particle reactor, while no increase in the recovery boilers NO_x emissions was detected. One of the key questions we were interested in was if more nitrogen exits with the smelt.

Figure 9 shows the cyanate content (mg N/L of green liquor) of the eight green liquors collected from the mill. Biosludge addition to black liquor clearly increased the amount of cyanate in the green liquor samples.

Figure 10 shows the amount of cyanate in the laboratory-made smelts as mg N/kg smelt from the as-fired black liquor we collected. This is consistent with the observed higher nitrogen content in the mill green liquors when biosludge was added to the black liquor. The laboratory-made smelts and the green liquor samples from the mill show roughly a 40% increase in cyanate when biosludge is added to black liquor. This increase corresponds to about 60% of the biosludge nitrogen. The remaining 40% most likely is released during pyrolysis, but does not apparently lead to any significant increase



11. NO_x concentration in lime kiln and NCG-boiler flue gas.

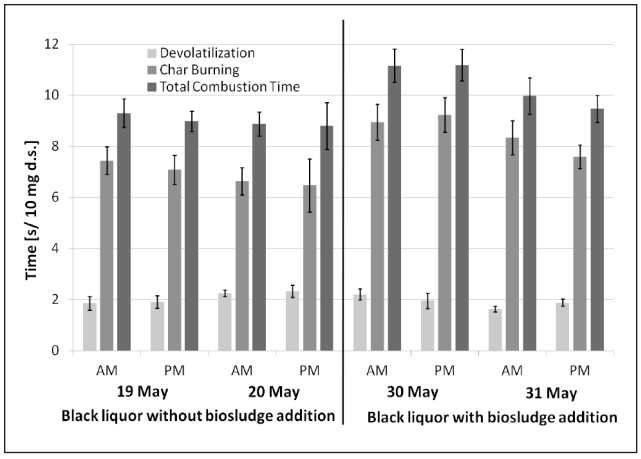
in NO in recovery boilers. This increase in cyanate could result in higher nitrogen emissions for the pulp mill, as cyanate reacts to form NH_3, which is then found in the tank vent gases, the MeOH, and NCG from the stripper, all of which ultimately are burned. Where they are burned can affect the overall mill NO_x emissions.

Figure 11 shows the NO_x concentration (in mg N/Nm_3) for the NCG boiler and the lime kiln and the biosludge addition to the black liquor. The NO_x data for the lime kiln and NCG boiler show a longer period to clearly establish if the addition of biosludge resulted in an increase in NO_x. We detected no clear increase in the average NO_x concentration in the lime kiln flue gas after biosludge addition. The lime kiln burns natural gas, and the high-volume, low concentration NCGs from recausticizing are fed to the lime kiln. NO_x emissions in the lime kiln could come, at least partially, from the nitrogen in the low concentration NCGs from recausticizing.

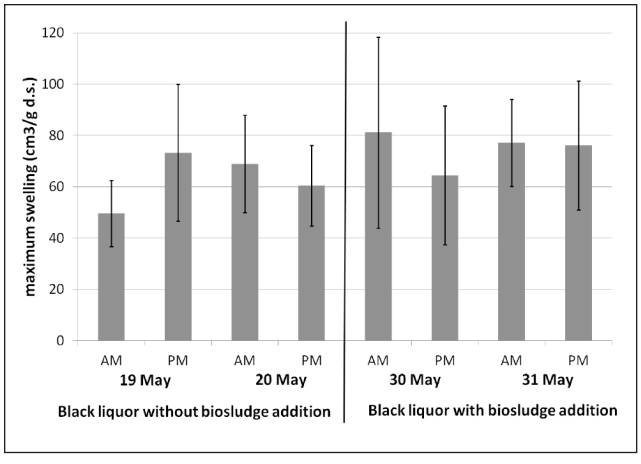
The NCG boiler burns the MeOH and the high concentration NCG from the stripper. The average NO_x concentration in the NCG boiler flue gas was 336 mg N/Nm_3 for the 19 days before biosludge was added to the black liquor and 407 mg N/Nm_3 for the 22 days after biosludge was added to the black liquor. This is a 21% increase after biosludge addition. The explanation is that the biosludge results in more cyanate in the smelt from the recovery boiler. This in turn results in more ammonia formed. A part of this NH_3 exits recausticizing with the white liquor and subsequently is collected in the dirty condensates from the pulp mill digesters and evaporators. This is then stripped and ends up in the MeOH and NCG from the stripper, both of which are burned in the NCG boiler.

Combustion characterization of the as-fired black liquors

With biosludge addition, no considerable difference was detected in the average devolatilization time for black liquor droplets burned at 1100°C in 3% O_2, but some increase was seen in the char burning time (**Fig. 12**). The high temperature and low oxygen ratio used in the combustion



12. Combustion times for black liquor samples at 1100°C and 3.3% O_2. Error bars represent 1 standard deviation for six replicate combustion tests.



13. Maximum swollen volume of black liquor samples at 1100°C and 3.3% O_2.

experiments led to the droplet igniting as soon as it entered the reactor. This, combined with extensive fuming during devolatilization, made it difficult to detect the appearance and disappearance of the flame. These two phenomena resulted in some uncertainties in the detected devolatilization times shown in Fig. 12.

Figure 13 shows the maximum swollen volume (in cm^3/g dry solids) for the black liquor samples with and without biosludge addition. We saw a very small difference in the average maximum swollen volume, but this increase is not expected to affect droplet combustion to any significant extent. The non-uniform nature of black liquor swelling and the use of a two-dimensional image for estimating volume result in a high standard deviation in the calculated maximum swollen volume. However, the average swollen volume has been used successfully in computational fluid dynamics modeling of black liquor recovery boilers and is considered useful in understanding the relative swelling tendency of black liquors and their subsequent behavior in flight.

Previous studies show that the addition of biosludge can prolong total combustion time [14,26], and that different biosludge addition levels have different effects on swelling [26]. Other researchers concluded that a 0.5 wt-% biosludge addition had no significant effect on the combustion properties of black liquor [27].

CONCLUSIONS

This research provides new insight into the fate of biosludge nitrogen in black liquor evaporation and combustion and how it might contribute to the overall nitrogen emissions of a kraft pulp mill. The addition of biosludge to black liquor increases the nitrogen content, and the biosludge nitrogen remains stable during the final stages of evaporation, thus increasing the nitrogen content of the as-fired black liquor. The higher nitrogen content does not result in clearly higher NO_x emission from the recovery boiler.

One new finding was that the increased nitrogen content of the as-fired black liquor resulted in an increase in cyanate formation, both in green liquor samples and laboratory-made smelts, which then results in more ammonia in the chemical recovery cycle. This increase in ammonia formation in the chemical recovery cycle explains the observed increase in the NO_x emissions from the NCG boiler after biosludge addition. This new data helps clarify the fate of biosludge nitrogen in the kraft recovery cycle when added to black liquor. **TJ**

ACKNOWLEDGMENTS

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LITERATURE CITED

1. Nichols, K.M., Thompson, L.M., and Empie, H.J., *Tappi J.* 76(1): 119(1993).
2. Nichols, K.M. and Lien, S.J., *Tappi J.* 76(3): 185(1993).
3. Iisa, K., Jing, Q., Conn, J., et al., *Int. Chem. Recovery Conf.*, Vol. 2, TAPPI PRESS, Atlanta, GA, USA, 1998, p. 763.
4. DeMartini, N., Forssén, M., Hupa, M., et al., *Int. Chem. Recovery Conf.*, TAPPI PRESS, Atlanta, 2004, p. 457.
5. Ververka, P.J., Nichols, K.M., Horton, R.R., et al., *Environ. Conf.*, TAPPI PRESS, Atlanta, 1993, p. 777.
6. Kymalainen, M., Forssen, M., and Hupa, M., *J. Pulp Pap. Sci.* 25(12): 410(1999).
7. Forssen, M., Hupa, M., Pettersson, R., et al., *J. Pulp Pap. Sci.* 23(9): J439(1997).
8. Aho, K., Hupa, M., and Vakkilainen, E., *Tappi J.* 77(5): 121(1994).
9. Aho, K., Hupa, M., and Nikkanen, S., *Tappi J.* 77(8): 182(1994).
10. Vainio, E., Brink, A., Demartini, N., et al., *J. Pulp Pap. Sci.* 36(3-4): 135(2011).
11. Demartini, N., Forssen, M., Niemela, K., et al., *TAPPI J.* 3(10): 3(2004).

12. Tamminen, T., Forssen, M., and Hupa, M., *TAPPI J.* 1(9): 25(2002).
13. Kymalainen, M., Forssen, M., Jansson, M., et al., *J. Pulp Pap. Sci.* 28(5): 151(2002).
14. Vähä-Savo, N., DeMartini, N., and Hupa, M. *Energy Fuels* 25(11): 4944(2011).
15. Kymalainen, M., Forssen, M., DeMartini, N., et al., *J. Pulp Pap. Sci.* (27)3: 75(2001).
16. Demartini, N., Forssen, M., Murzin, D.Y., et al., *J. Pulp Pap. Sci.* 30(12): 329(2004).
17. Janka, K., Ruohola, T., Siiskonen, P., et al., *TAPPI J.* 81(12): 137(1998).
18. Forssen, M., Kilpinen, P., and Hupa, M., *TAPPI J.* 83(6): 56(2000).
19. Saviharju, K., Aho, K., Forssén, M., et al., *Int. Chem. Recovery Conf.*, TAPPI PRESS, Atlanta, 2007, p. 589.
20. Salmenoja, K., Forssén, M., and Hupa, M., *Int. Chem. Recovery Conf.*, TAPPI PRESS, Atlanta, 2007, p. 583.
21. Kymalainen, M., Holmstrom, M., Forssen, M., et al., *J. Pulp Pap. Sci.* 27(9): 317(2001).
22. Valttila O., Jarvinen, R., Rainio, K., et al., *TAPPI Int. Chem. Environ. Conf.*, TAPPI PRESS, Atlanta, 1994, p. 49.
23. DeMartini, N., "Determination of cyanate in kraft green liquor," M.S. thesis, Åbo Akademi University, Department of Chemical Engineering, Turku, Finland, 2001.
24. Björkvik, T., "Measurement of sulfur release from black liquor droplets in a single particle reactor," M.S. thesis, Åbo Akademi University, Finland, 2010.
25. Hupa, M., Solin, P., and Hyoty, P., *J. Pulp Pap. Sci.* 13(2): J67(1987).
26. Demartini, N., Monedero, E., Yrjas, P., et al., *TAPPI J.* 9(9): 29(2010).
27. Harila, P. and Kivilinna, V.-A., *Water Sci. Technol.* 40(11-12): 195(1999).

ABOUT THE AUTHORS

This work was part of a larger project having to do with the fate of nitrogen in kraft pulping and chemical recovery. The fate of biosludge nitrogen has been studied previously, but no concrete findings have yet been published. This work complements previous work by Maritta Kymäläinen and Nikolai DeMartini.

The most difficult aspect of our research was figuring out what the black liquor flows were in the evaporation.

Biosludge has no clear effect on combustion properties of black liquor and we found that the added nitrogen from biosludge does not show any increase in NOx formation at the recovery boiler.

As a result of this research, mills will have information available to them about what happens to the combustion properties of black liquor when biosludge is added and the fate of biosludge nitrogen. Our next step is to study whether electrostatic precipitator ash addition to black liquor influences the fate of nitrogen in black liquor combustion.

Vähä-Savo

DeMartini

Hupa

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