Fuel nitrogen release during black liquor pyrolysis

Part I: Laboratory measurements at different conditions

Kaisa Aho, Mikko Hupa, and Esa Vakkilainen

ABSTRACT: Fuel nitrogen release during black liquor pyrolysis is high. There is only minor release during the drying stage. Ammonia is the main fixed nitrogen species formed. The rate of fixed nitrogen release increases with increasing temperature. The level of fixed nitrogen released by birch liquor is almost twice the level for pine liquor. Assuming complete conversion to NO, fixed nitrogen yields gave NO concentrations near typically measured values for flue gases in full scale recovery boilers.

KEYWORDS: Betula, black liquors, combustion, fuels, measurement, nitrogen compounds, pinus, pyrolysis, release, temperature.

Nitrogen oxide emissions from black liquor recovery boilers typically vary in the range from 50 ppm to 100 ppm (40–90 mg NO_2/MJ). There is no ready explanation for the physical and chemical mechanisms for formation of these emissions in a recovery furnace. Recent research has indicated that a major part of this NO emission would be "fuel NO_x" originating from the organic nitrogen compounds in the black liquor. Only a minor part would be "thermal NO_x" from the molecular nitrogen in the combustion air *(1–3)*. Previous assumptions were that thermal NO_x increased under conditions of very high furnace temperatures. This would typically be the case when firing liquors with very high dry solids content *(4, 5)*. Actual data provides conflicting reports, however, so there is no complete understanding of the role of the fuel NO_x vs. thermal NO_x *(6)*.

The purpose of this work was to gain more detailed information about the behavior of the fuel nitrogen in black liquor combustion. The work focused on the pyrolysis or devolatilization of the combustion process. Devolatilization is the stage at which the majority (typically 50–80%) of the liquor organics release from a fuel particle or droplet as gaseous species due to the rapid destruction of the organic macromolecules in the liquor *(7)*. In this paper, we use the terms devolatilization and pyrolysis interchangeably with no difference in their meaning.

The starting point for this work was the assumption that a significant part of the liquor nitrogen would release during the pyrolysis process as reactive nitrogen intermediates such as hydrogen cyanide or ammonia. We suspected that these intermediates were a major source for the NO_x found in recovery boiler flue gases. In the first part of our work, we studied the release of the fuel nitrogen at a variety of different conditions using liquor from one softwood and one hardwood. The main intent was to identify and quantify the nitrogen compounds released during pyrolysis of single black liquor droplets at different temperatures in an oxygen-free environment.

The second part of this work following in a future issue of this journal focuses on the variations between different liquors in fuel nitrogen release behavior and in the tendency

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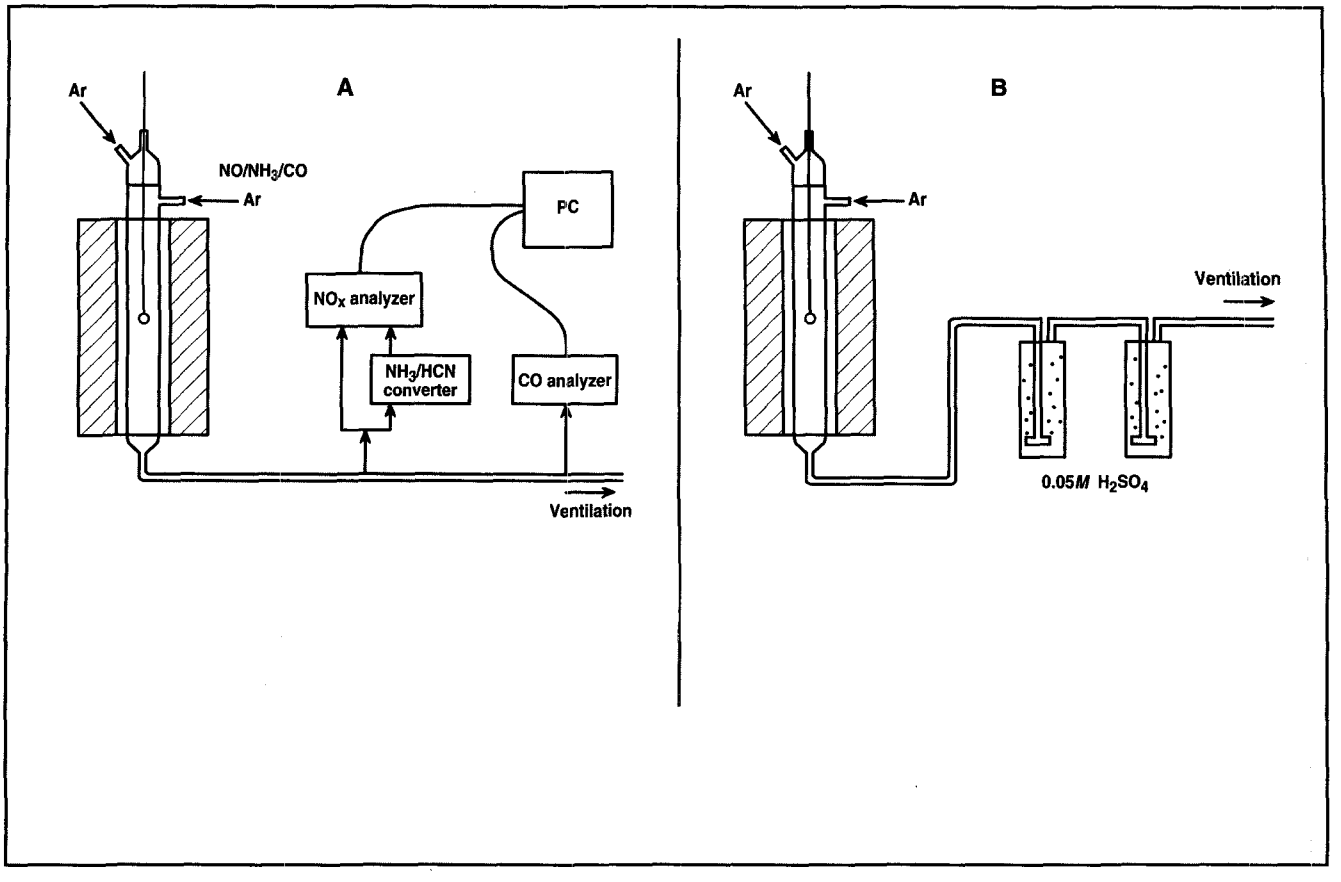
1. Experimental technique to determine release of nitrogen compounds during black liquor pyrolysis



to form NO_x in a full-scale recovery boiler *(8)*.

Experimental

Black liquor samples

The two black liquors studied in this work were laboratory cooked pine having a nitrogen content of 0.12% and 62% dry solids and laboratory cooked birch with nitrogen content 0.17% and 51% dry solids. There were four other liquors which either were laboratory cooked or were mill black liquors. We used these to verify the results.

Experimental apparatus and test conditions

We heated black liquor droplets in a laboratory tube furnace in argon. We measured the NO_x, NH_3, and HCN released during this heating. We followed the progress of the liquor devolatilization by measuring the content of carbon monoxide of the gases produced. **Figure 1** shows the experimental apparatus. The pyrolysis reactor was the same as other investigators previously used for sulfur release experiments *(9)*.

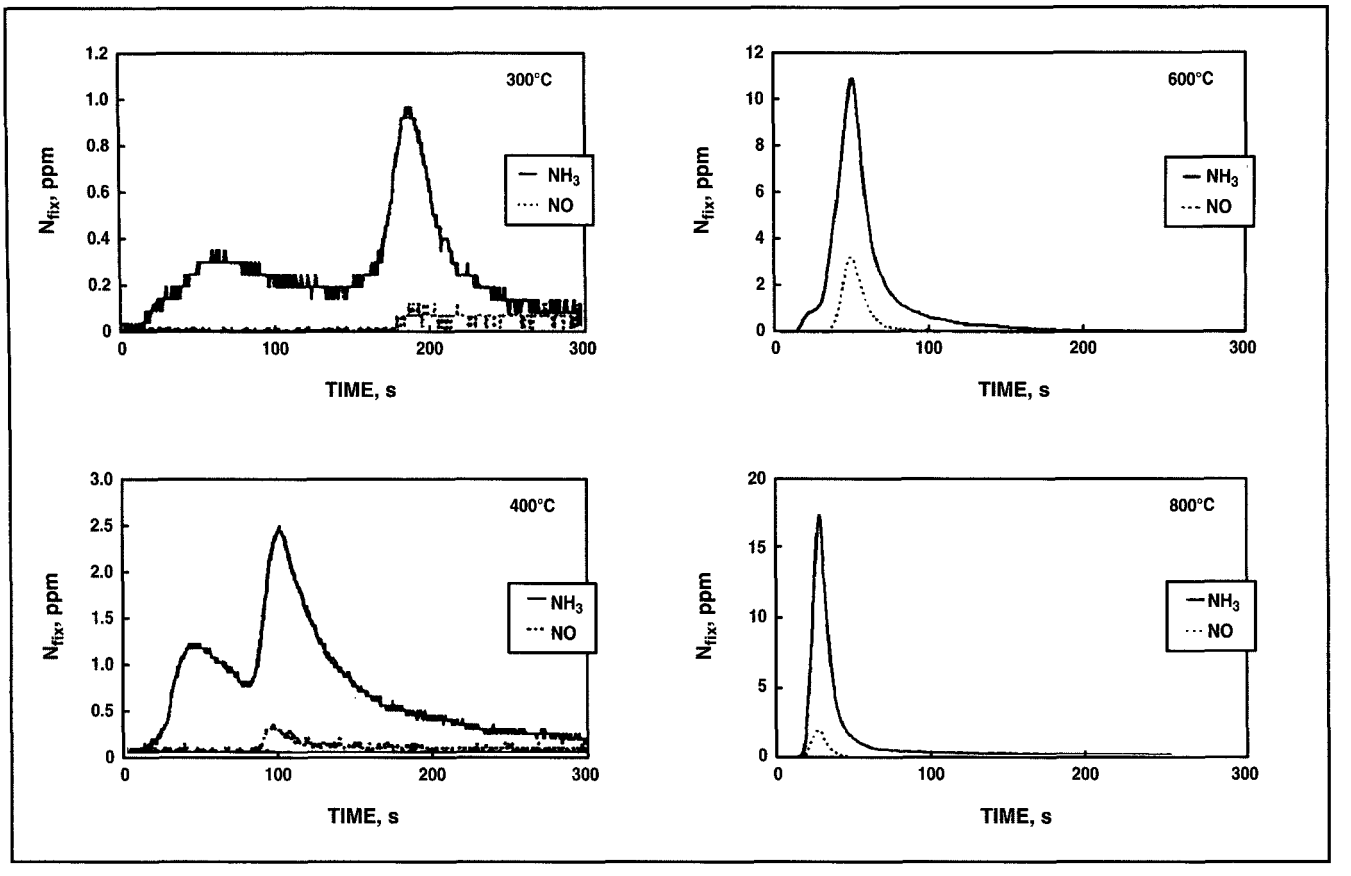
In each experiment, we suspended a single droplet of liquor on a platinum hook, lowered it into the reactor, and removed it after 300 s. We weighed the droplets before and after the pyrolysis. We repeated the measurements 4–15 times for an average of 9.3 times using droplet sizes ranging from 35 mg to 80 mg. The gas stream through the reactor was 180 L/h. The furnace temperature varied between 300°C and 950°C.

We conducted additional pyrolysis tests for larger liquor samples in a muffle furnace. In this case, we determined the amounts of volatile compounds and the amounts of fuel nitrogen released by treating the black liquor in a crucible for 1 h at 400°C. We determined the weight as

I. Pyrolysis yield of N_{fix} compounds in mg N/100 g BLS

Sample no.	*Temp., °C*	*NH3 grab sample*	*NH_3+HCN NO_x - anal. (1)*	*NH_3+HCN+NO NO_x - anal. (2)*
1 (Pure pine)	800	14.8	14.0	16.7
2 (Pure birch)	800	28.3	26.4	29.6
3	800	21.6	19.8	22.7
4	600	11.3	8.8	18.9
4	800	15.0	12.4	14.6
5	800	25.0	17.9	20.0
6	800	14.2	12.2	14.9

2. Release of nitrogen compounds during pyrolysis of a birch liquor at 300–800°C



well as the carbon, hydrogen, and nitrogen content of the samples before and after the tests.

Analytical methods

We analyzed NO content of the pyrolysis gases with a commercially available chemiluminescence based NO_x analyzer. We calibrated the unit for a range of 0 ppm to 100 ppm by diluting 200 ppm NO–calibration gas with argon. The analyzer measured the sum of NO and NO_2. Since preliminary tests had shown that the amount of NO_2 released during pyrolysis was insignificant, we did not measure it separately.

A NO_x analyzer with a commercial converter, as diagram A of Fig. 1 shows, analyzed the sum of NH_3 and HCN in the pyrolysis gases. A small oxygen stream connected to the cold gas stream before the converter delivered 3–5 L/h. The operating temperature of the converter was 750°C. Diluting with calibrating gases containing 100 ppm NH_3 and 360 ppm HCN, respectively, in argon calibrated the equipment for the range of 0 ppm to 100 ppm. In small concentrations, the conversion to NO was complete in both cases.

For determination of the content of NH_3 separately, we collected samples by leading the pyrolysis gas (40 L/h) through two gas washing bottles filled with 100 mL 0.05*M* H_2SO_4 as diagram B of Fig. 1 indicates. A commercially available ion selective electrode measured the NH_3 content of the scrubber solution.

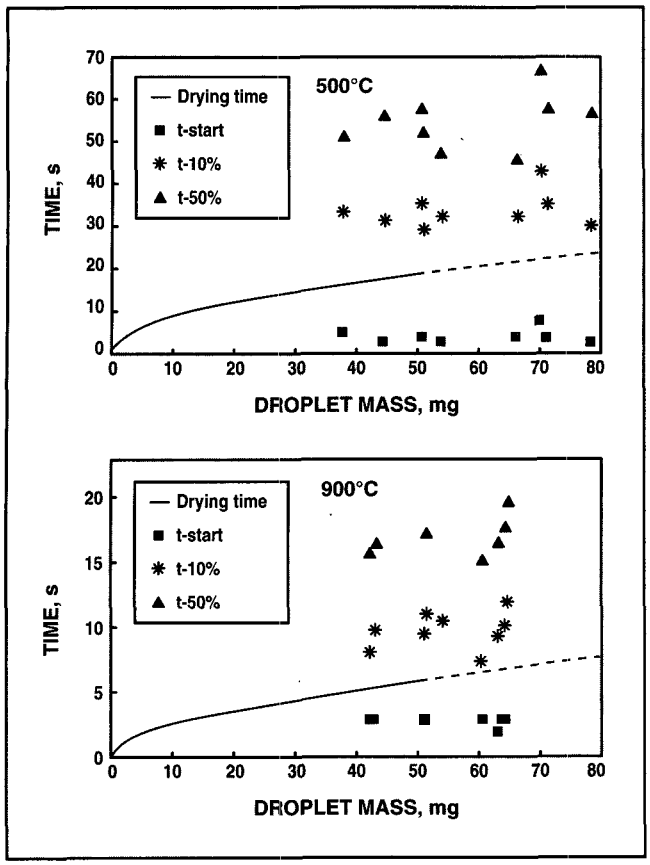
A commercial analyzer measured the C, H, and N contents of liquors and char residues by burning the sample in pure oxygen at 950°C. An infrared detector for determining C and H contents analyzed the combustion gases. The nitrogen content of liquors was calculated by reducing the NO_x compounds of the gases to N_2 for detection by a thermal conductivity cell.

Results and discussion

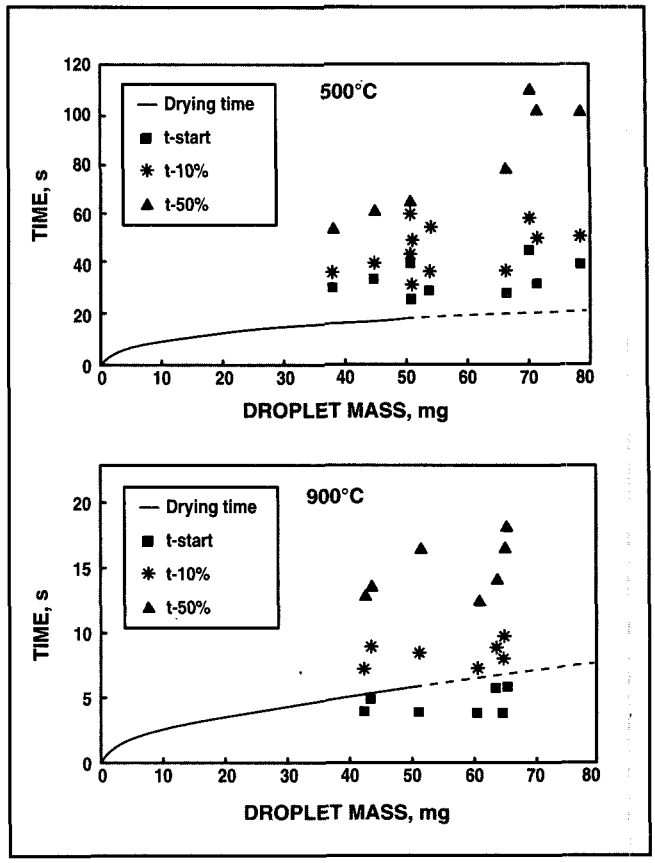
Nitrogen compounds released during black liquor pyrolysis

The known intermediates of fuel-bound nitrogen formed during combustion of fossil fuels are NH_3 and HCN. We determined the significance of these compounds during black liquor pyrolysis by analyzing separately the NH_3 concentration itself and the total of NH_3 plus HCN concentrations using two independent methods. Converting NH_3 and HCN to NO and measuring allowed determination of these materials. We determined NH_3 alone in grab samples absorbed in an acidic solution. **Table I** gives results for six liquor samples at one pyrolysis temperature and for one liquor

3. Calculated drying time and release of NH_3 during pyrolysis of birch liquor at 500°C and 900°C



4. Calculated drying time and release of NO during pyrolysis of birch liquor at 500°C and 900°C



sample at two temperatures. The table provides a comparison of NH_3 measurements based on absorbed grab samples and fixed nitrogen (N_{fix}) analysis based on integration of the continuous NO_x concentration signal after an oxidative converter. Integration time was 300 s.

The results indicate that NH_3 found in the absorption solution was slightly higher than the sum of NH_3 and HCN for all liquors studied. These small differences are not significant and probably result from inaccuracies in the analytical procedure. It is therefore possible to conclude that very little or no HCN forms or, alternatively, all HCN which initially forms converts to NH_3 before the sampling point.

Besides NH_3, small amounts of NO and some molecular nitrogen released during the pyrolysis of black liquor. In this paper, N_{fix} collectively refers to the sum of HCN, NH_3, and NO as fixed nitrogen compounds.

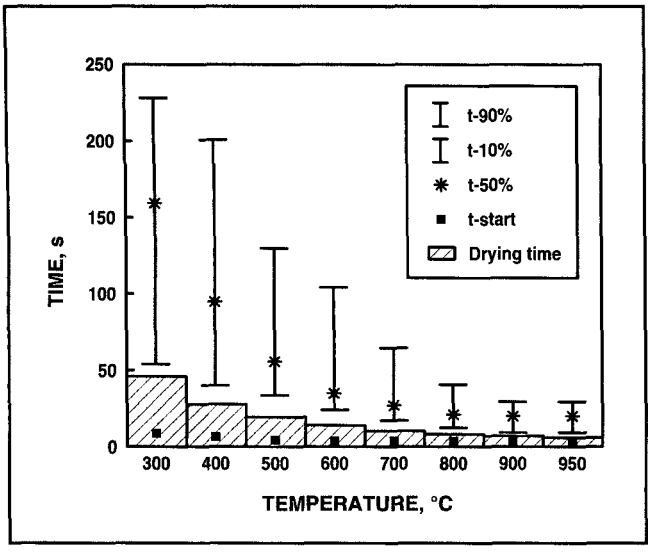
Nitrogen release rate

Figure 2 shows the concentration of N_{fix} compounds released vs. time at 300–800°C for the birch liquor. At low temperatures, the rate of nitrogen release is rather slow. There are clearly two separate peaks of NH_3. This indicates that some nitrogen releases as NH_3 during the drying of the droplet. **Figure 3** examines this more closely by showing estimated drying times for the black liquor droplets together with the measured results of NH_3 release. The figure shows the drying time, the starting time, the time for release of 10% of the total NH_3, and the time for release of 50% of the NH_3. Calculation of the drying time curves used a simple heat transfer model of a black liquor droplet drying process *(10)*. **Figure 4** shows corresponding data for NO release.

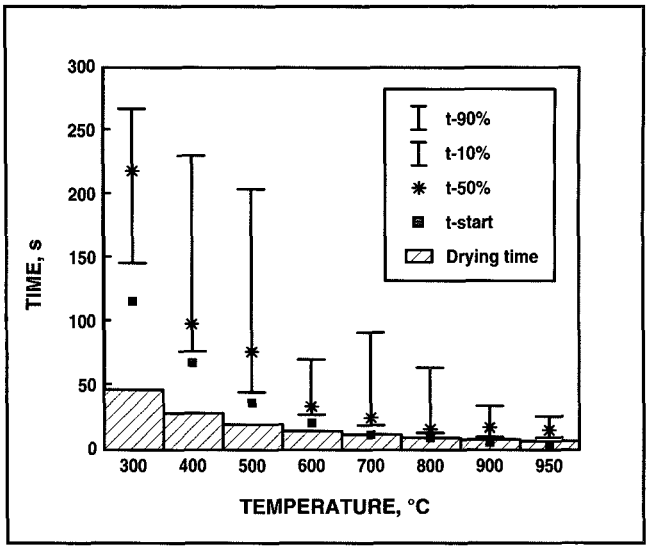
Figures 5 and 6 summarize release times of NH_3 and NO at temperatures of 300–950°C. In these figures, the vertical lines indicate the time periods for release of 80% (from 10% to 90%) of the total NH_3. The squares indicate the detection time for the first signal. The asterisks indicate the times for release of 50% of the total NH_3. The results suggest that the main part of the release of N_{fix} compounds occurs during the pyrolysis process after completion of the drying. At high temperatures, the drying and pyrolysis partially overlap, and pyrolysis obviously begins before the droplet is completely dry.

We evaluated the times for the release of 50% of the NH_3 and NO, t_{50}, for both the pine and the birch liquor by integrating from the starting point of pyrolysis to the point of release of one half of each of the respective nitrogen compounds. We estimated apparent activation energies (E_a) for each release process

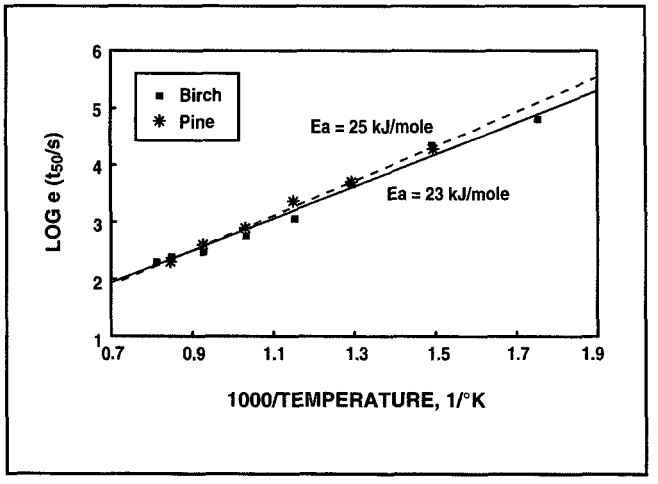
5. Calculated drying times and release of NH_3 during pyrolysis of birch liquor at 300–950°C



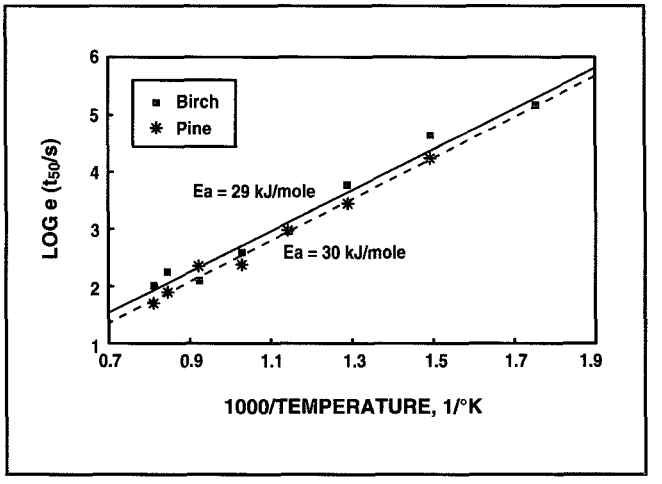
6. Calculated drying times and release of NO during pyrolysis of birch liquor at 300–950°C



7. Arrhenius plot for NH_3 release from pine and birch liquors within the range 300–950°C for droplet size 40–50 mg



8. Arrhenius plot for NO release from pine and birch liquors within the range 300–950°C for droplet size 40–50 mg



using the slope of the Arrhenius type plots shown in **Fig. 7** for NH_3 release and in **Fig. 8** for NO release. The apparent activation energy values for NH_3 release were 23 kJ/mole for birch liquor and 25 kJ/mole for pine liquor. Corresponding values for the NO release were 29 kJ/mole and 30 kJ/mole.

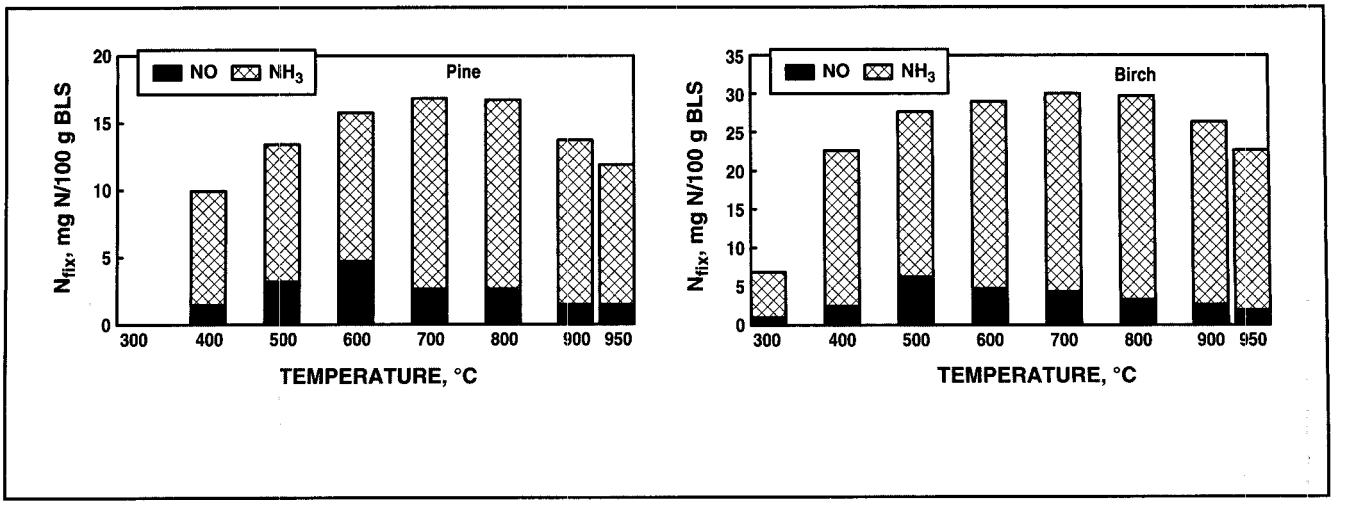
We obtained these results in the same way as previously shown for sulfur release from black liquor pyrolysis *(9)*. The estimated activation energy for sulfur release was 26 kJ/mole in the temperature range of 350°C to 675°C. This suggests that nitrogen and sulfur release processes during pyrolysis closely relate to one another. In addition, heat transfer from the surroundings to the liquor particle determines the nitrogen and sulfur release *(9)*.

Total yield of N_{fix} during pyrolysis

Figure 9 shows the total yields of N_{fix} per 100 g black liquor solids (BLS). These data come from an integration of the release vs. time curves similar to those of Fig. 2. Integration time in these measurements ranged to 300 s because of the slow rate of pyrolysis at low temperatures. The amount of N_{fix} released at temperatures of 300°C and 400°C could in reality be somewhat bigger. After 300 s, however, the nitrogen levels were too low for detection by the analytical method used.

Figure 10 compares the results of both wood species. It indicates that the level of N_{fix} released from the birch liquor was almost twice the level from the pine liquor. The yield vs. temperature curves have a

9. Total release of N_{fix} compounds during pyrolysis at different temperatures



similar shape for both liquors with a maximum at 700–800°C. At higher temperatures, the release of N_{fix} decreases. This may result from increased secondary reactions in the pyrolysis gases where NH_3 and NO may convert to molecular nitrogen.

Fuel nitrogen balance during pyrolysis

To close the fuel nitrogen balance during the black liquor pyrolysis, some additional tests were necessary. In these tests, we determined the total fuel nitrogen released by analyzing the nitrogen content in the fuel before the pyrolysis, N_{fuel}, and in the char after the pyrolysis, N_{char}. At the same time, we also analyzed the C and H content in the liquor and char. This procedure allowed determination of the amount of total fuel nitrogen released during pyrolysis, N_{vol}, using the following materials balance:

$$N_{vol} = N_{fuel} - N_{char} \quad (1)$$

In addition to the fixed nitrogen compounds, N_{fix}, N_{vol} contains any molecular nitrogen formed from the fuel nitrogen as follows:

$$N_{vol} = N_{fix} + N_2 \quad (2)$$

Table II shows the analytical results before and after pyrolysis of birch liquor. The original liquor composition was 37.0% C, 4.32% H, and 0.170 ± 0.010% N. The first four columns give results obtained by analyzing the char samples from the single droplet tests in the tube furnace at four different furnace temperatures. In these tests, one can close the nitrogen balance by comparing the N_{vol} obtained by char analysis, on one hand, and by analyzing the N_{fix} species in the pyrolysis gases, on the other hand. We assumed the "missing" released nitrogen species was molecular nitrogen whose amount it was possible to calculate. The analysis of nitrogen in the single char residue particles was, however, fairly inaccurate. The data in the table are only preliminary and need validation with more accurate methods.

The last column in Table II gives corresponding analysis values for pyrolysis of much larger birch liquor samples at 400°C in a muffle furnace. The typical sample size was 2–3 g. For these muffle furnace tests, the released nitrogen gases were undetectable, but the char analysis was more reliable than for the single particle experiments in the tube furnace.

According to these tests, the volatiles yield varied from 16% to 49%, depending on the furnace temperature. Total volatilized fuel nitrogen varies for this liquor between 20% and 40% of the original nitrogen in the black liquor solids depending on temperatures. A significant part of this volatilized nitrogen obviously releases as molecular nitrogen, N_2.

Conclusions

There was a significant part of the fuel nitrogen released during the pyrolysis process and only a minor part of the nitrogen released during the drying stage.

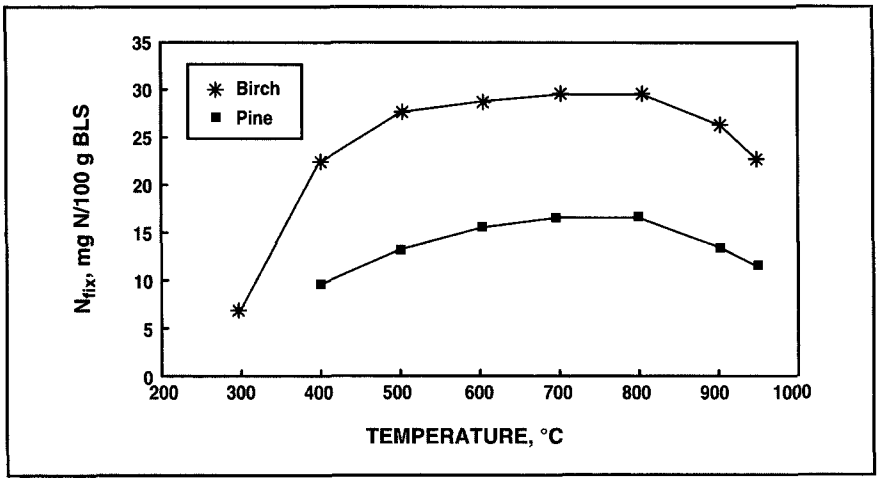
The main N_{fix} species formed was NH_3. There was no formation of HCN, which is the common nitrogen intermediate in fossil fuel pyrolysis. Another possibility is that all HCN initially formed converted to NH_3 in the pyrolysis gases before reaching our analyzer. Besides NH_3, there was also release of small amounts of NO and certainly molecular nitrogen.

There was a total of 15-20% of fuel nitrogen release as N_{fix} compounds, NH_3 and NO, during pyrolysis of the two liquors studied. The rate of release of N_{fix} increased with increasing temperature.

The level of N_{fix} released from birch liquor was nearly twice the level released from pine liquor. The yield was 25–30 mg N/100 g BLS for the birch liquor and 13–17 mg N/100 g BLS for the pine liquor in the temperature range of 500°C to 900°C.

These yields are large enough to

10. Total release of N_{fix} during pyrolysis of black liquor at different temperatures



II. Analysis of char residues

	Single droplet pyrolysis				Muffle furnace pyrolysis
	300°C	500°C	600°C	800°C	400°C
Vol % of BLS	16.2	36.2	36.8	49.3	36.9
C, % in char	36.6	35.6	34.0	30.6	33.9
H, % in char	3.86	1.70	0.88	0.61	1.15
N, % in char	0.16	0.18	0.18	0.19	0.168 ± 0.024
C_{vol}, % of C in BLS	17.2	38.5	42.0	58.0	42.2
H_{vol}, % of H in BLS	25.1	74.9	87.1	92.8	83.2
N_{char}, % of N in BLS	80.5	68.8	65.1	56.7	62.4
N_{vol},% of N in BLS (100 - N_{char})	19.5	31.2	34.9	43.3	37.6
N_{fix}, % of N in BLS	3.9	16.3	16.9	17.4	
N_2, % of N in BLS (N_{vol} - N_{fix})	15.6	14.9	18.0	25.9	

produce typical NO_x emission levels from a recovery boiler, if one assumes a complete conversion of this N_{fix} to NO in the oxidative parts of the furnace.

The maximum levels of N_{fix} release occurred in the temperature range of 600°C to 800°C. At temperatures higher than 800°C, a part of the N_{fix} originally released probably formed molecular nitrogen in the pyrolysis gas stream to give a lower total N_{fix} release.

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