Fuel nitrogen release during black liquor pyrolysis

Part 2: Comparisons between different liquors

Kaisa Aho, Mikko Hupa, and Samuli Nikkanen

ABSTRACT: This continuation of earlier work reports fuel nitrogen release for black liquors at two temperatures during pyrolysis of single droplets in an oxygen–free environment. Approximately half of the 20–60% fuel nitrogen released was ammonia and half was molecular nitrogen. The total amount of fixed nitrogen released during pyrolysis was almost linearly proportional to the liquor nitrogen content. The yield of fixed nitrogen for birch liquors was significantly higher than for pine liquors, and the yield for bagasse liquor was extremely high.

KEYWORDS: Black liquors, combustion, emission, fuels, furnaces, heat treatment, nitrogen compounds, pyrolysis, release, spent liquors.

Part 1 of this work indicated that nitrogen oxide emissions from black liquor recovery boilers typically range from 50 ppm to 100 ppm (40–90 mg NO_2/MJ) *(1)*. 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 *(2–4)*. 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 *(5, 6)*. Actual data provides conflicting reports, however, so there is no complete understanding of the role of the fuel NO_x vs. thermal NO_x *(7, 8)*.

The purpose of this work was to gain more detailed information about the behavior of the fuel nitrogen in black liquor combustion. The first part of this work showed that a significant part of the liquor nitrogen releases during the pyrolysis or devolatilization stage *(1)*. Fixed nitrogen species, i.e., all nitrogen species except N_2, constitute a major part of this release, and the remainder is molecular nitrogen.

The fixed nitrogen species readily oxidize to nitric oxide, NO. They are common precursors of NO. The main fixed nitrogen species detected in the product gases of the oxygen–free pyrolysis was ammonia. Roughly 20% of the fuel nitrogen released as ammonia during pyrolysis of the two liquors studied. There was no evidence of hydrogen cyanide, the common nitrogen intermediate in fossil fuel pyrolysis. Besides ammonia, some nitrogen oxide, NO, also occurred although the pyrolysis took place in an inert gas atmosphere.

The total yield of fixed nitrogen species released during pyrolysis of a soft wood liquor sample was 13–17 mg N/100 g of black liquor solids (BLS). For a hardwood liquor, the corresponding yield was 25–30 mg N/100 g BLS.

This second part of the work focused on the differences between liquors in their fuel nitrogen release behavior and in their tendency to form nitrogen oxides in a full-scale recovery boiler. We analyzed a total

Aho is research engineer at A. Ahlstrom Corp., P.O. Box 184, Varkaus, SF 78201, Finland; Hupa is professor at Abo Akademi University, Chemical Engineering Dept., Lemminkaisenkata 14–18B, Turku, SF 20502, Finland; and Nikkanen is sales manager at A. Ahlstrom Corp., P.O. Box 184, Varkaus, SF 78201, Finland.

I. Properties of the liquors studied

Sample	Description	Dry solids, %	Higher heating value, MJ/kg, on dry solids	Nitrogen, % on dry solids
1	Pure pine, laboratory cook	62.0	16.86	0.124 ± 0.025
2	Pure birch, laboratory cook	50.9	15.57	0.170 ± 0.010
3	Pure birch, laboratory cook with LHT	64.1	15.59	0.166 ± 0.007
4	Pine, mill	66.6	14.93	0.126 ± 0.007
5	Birch, mill	66.6	15.07	0.150 ± 0.020
6	Mixed: 50% pine and 50% birch	68.1	14.71	0.141 ± 0.013
7	Mixed: 50% pine and 50% birch with LHT	65.3	14.85	0.140 ± 0.014
8	Pine, mill	65.6	14.96	0.120 ± 0.009
9	Pine, mill with LHT	59.1	14.52	0.106 ± 0.014
10	Bagasse, mill	71.7	14.90	0.478 ± 0.028

II. Elemental composition of liquors studied

Sample	Na, %	K, %	Cl, %	S, %	C, %	H, %	Balance, %
1	15.8	0.16	0.10	4.04	40.9	4.03	34.9
2	16.2	0.15	0.09	4.10	37.0	4.32	38.0
3	16.2	0.19	0.09	3.83	36.3	4.21	39.0
4	17.3	1.65	0.15	4.32	36.2	3.86	36.4
5	17.9	1.61	0.16	4.65	33.6	3.65	38.3
6	16.9	1.39	0.12	4.78	33.3	3.75	39.6
7	16.8	1.54	0.18	4.73	33.3	3.63	39.7
8	20.1	1.18	-	4.80	35.6	3.44	34.8
9	22.5	1.33	-	2.66	37.7	2.66	33.1
10*	18.4	0.72	0.17	0.06	37.9	4.08	36.5

*Si content: 1.70% on dry solids

of ten liquors with different origins by laboratory pyrolysis. The liquors included both mill liquors and liquors produced by well–controlled laboratory cooking. The study also included three liquors treated in a special liquor preheating system. This paper presents the results of the laboratory measurements with these ten liquors together with emission data from full-scale recovery boilers using similar fuels.

Experimental

Black liquor samples

Three of the black liquor samples studied represented different laboratory pulping conditions. Seven samples were mill liquors. Samples 1 and 2 were identical to those studied extensively in the first part of this work. Samples 3, 7, and 9 were heat–treated liquors from original samples 2, 6, and 8. A thermal depolymerization process changes the composition and properties of black liquor in the liquor heat treatment (LHT) *(9)*. **Table I** shows the properties of the liquor samples, and **Table II** provides the elemental composition of the liquors. The amounts in the column designated "balance" in Table II represent material that is mostly oxygen.

Experimental apparatus and test conditions

Black liquor droplets underwent heating in a laboratory tube furnace in argon with measurement of the nitrogen compounds, NO and NH_3 (collectively called N_{fix}), released during this heating. The experimental arrangement and the analytical methods were the same as previously used *(1)*.

In this work, the measurements used only two furnace temperatures, 600°C and 800°C. Integration time in these tests was 120 s. Each measurement experienced replication 4–15 times for an average of 8.5 with different droplet sizes of 35–80 mg.

There were additional pyrolysis tests for larger liquor samples in a muffle furnace. Treating the liquor samples in a crucible for 1 h at 400°C allowed determination of the amount of total volatiles and the amount of fuel nitrogen released. There were measurements of the weight and the carbon, hydrogen, and nitrogen content of the samples before and after the tests.

Emission measurements in four mills

Our organization made several process studies during 1990–92 *(8)* with measurement of NO_x emissions of recovery boilers. This work presents the results of five studies in four mills using different wood species as raw material for the pulping process. It also shows the results before and after LHT *(9)*.

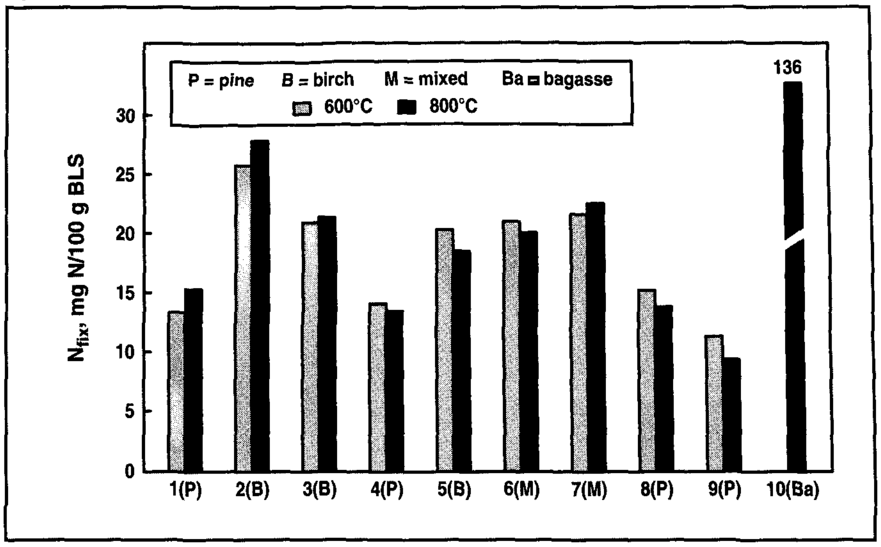
Study 1 in mill 1

The objective of these experiments was to study the effect of LHT on boiler operation and emissions. Wood species was also a variable. Data collection occurred over five 8–10 h periods. Three of these represent pine liquor use, and two periods cover birch liquor use. During four periods, the burned liquor was heat-treated, high-solids liquor. The dry solids content was 75–79%. One pine liquor period was the reference period without LHT. It had dry solids content of 68%.

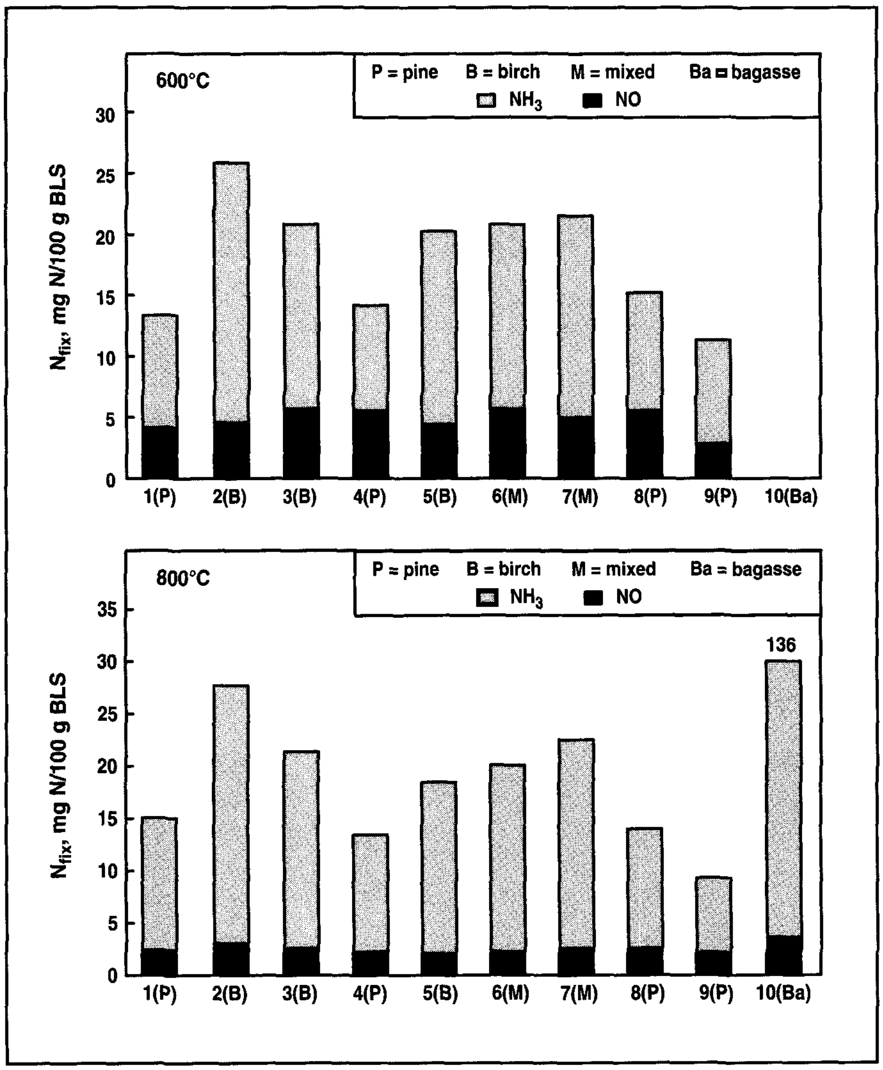
Study 2 in mill 2

In this case, the intent was to study the effect of air distribution on boiler operation and emissions. Both pine and birch liquors used the same air modes for testing. Data collection covered fourteen 8-h periods. Seven of these involved pine liquors, and seven involved birch liquor. Dry solids contents of liquors were 64–68%.

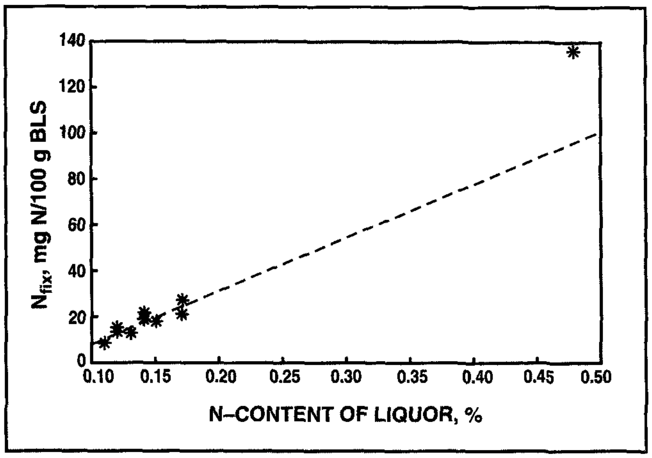
1. Total release of fixed nitrogen during pyrolysis of different black liquors at 600°C and 800°C



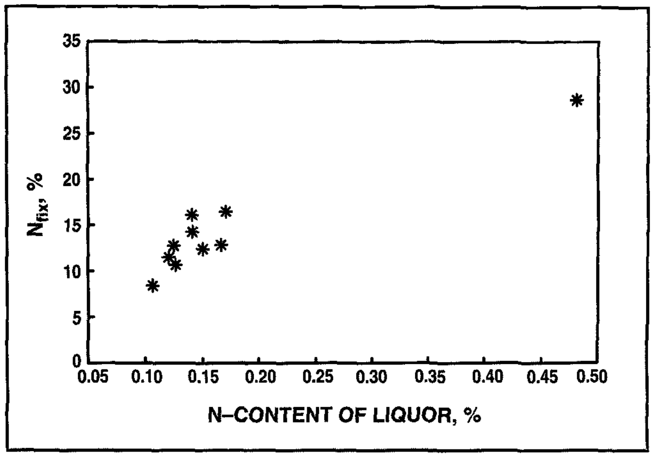
2. Release of fixed nitrogen compounds during pyrolysis of different black liquors at 600°C and 800°C



3. Total release of fixed nitrogen during black liquor pyrolysis at 800°C as a function of liquor nitrogen content



4. Conversion of fuel nitrogen to N_{fix} as a function of liquor nitrogen content at 800°C



Study 3 in mill 2

This study also examined the influence of the LHT on NO_x emissions. The LHT experiments covered two 9-h test periods. There was a comparison of the results with the results of the test period before LHT installation. Wood species during these tests was pine. Dry solids contents of liquors were 72% in the LHT periods and 66% in the reference period.

Study 4 in mill 3

Here the objective was to adjust and optimize the boiler operation. Data collection encompassed eight 4–14-h periods. The wood species during these tests was eucalyptus. The dry solids content of the combustion liquor was 63–64%.

Study 5 in mill 4

The purpose of this study was to find the operation mode required for the best reduction of NO_x. The tests used two modes of firing in the recovery boiler. One case involved firing the auxiliary fuel with black liquor, and the other involved operation with black liquor only. The other variables in the test were air distribution, primary and secondary air temperatures, and black liquor temperatures. The wood species during these tests was redwood. The dry solids content of the combustion liquor was 71–73%.

Results and discussion

Liquor comparison at two pyrolysis temperatures

Figure 1 shows the amount of N_{fix} released during pyrolysis at the studied temperatures, 600 and 800°C. There are systematic variations at both temperatures in the yield of N_{fix} released between different wood species. For pine liquors (samples 1, 4, 8, and 9), the yields of N_{fix} are lowest at 9–15 mg N/100 g BLS. The corresponding values for birch liquors (samples 2, 3, and 5) are 18–27 mg N/100 g BLS. The results for mixed liquors (samples 6 and 7) are of the same order of magnitude as for the birch liquors. The yield of N_{fix} from the liquor designated sample 10 is exceptionally high—136 mg N/100 g BLS. This sample is a liquor from pulping of bagasse.

The order of the liquors for their tendency for N_{fix} release was identical in the tests at both 600°C and 800°C. **Figure 2** shows the nitrogen compounds NH_3 and NO released at 600°C and 800°C separately. The proportional amount of NO in the N_{fix} was smaller at 800°C for all liquors. The level of NO does not seem to depend on the type of liquor.

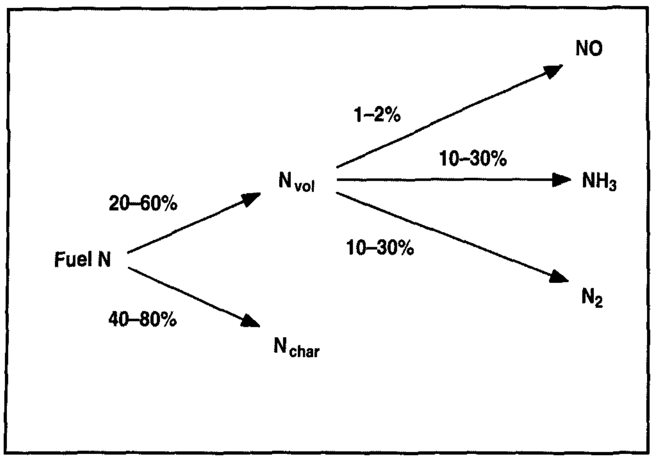
Considering the sample pairs of 2 and 3, 6 and 7, and 8 and 9 shows the effect of LHT on the release of N_{fix}. Samples 3, 7, and 9 represent heat-treated samples from original samples 2, 6, and 8. The N_{fix} released from the heat-treated samples 3 and 9 was less than the original samples at both studied temperatures. Only with the sample pair 6 and 7 was N_{fix} release somewhat lower for the original sample compared to the heat-treated sample. Sample pair 6 and 7 comes from a mill, however. The elemental analysis reveals that heat treatment had not operated normally. In successful heat treatment the liquor sulfur content decreases significantly. This seems not to be the case for liquor 7.

Release of N_{fix} as a function of black liquor nitrogen content

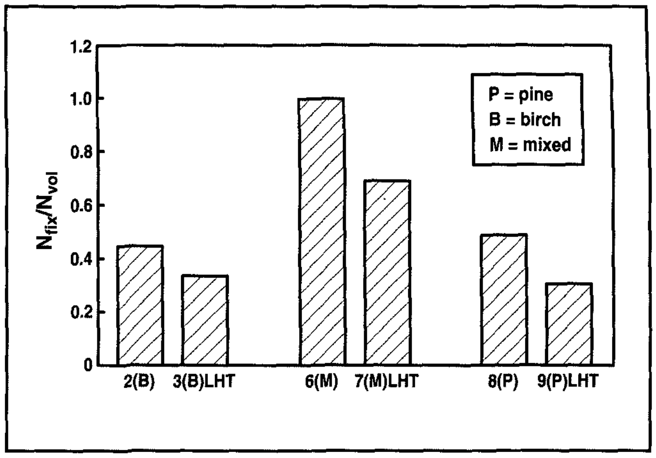
Figure 3 shows the N_{fix} release during the pyrolysis of the different liquors at 800°C as a function of N content of the liquor. Calculation of the regression does not consider the exceptional bagasse liquor. The results suggest that N_{fix} released during pyrolysis increases with increasing liquor nitrogen content.

Figure 4 shows the conversion of fuel nitrogen to N_{fix} as a function of liquor nitrogen content at 800°C. The conversion of fuel nitrogen to N_{fix} during pyrolysis varied between approximately 10% and 30% and appeared slightly higher for liquors with a higher nitrogen content. Due

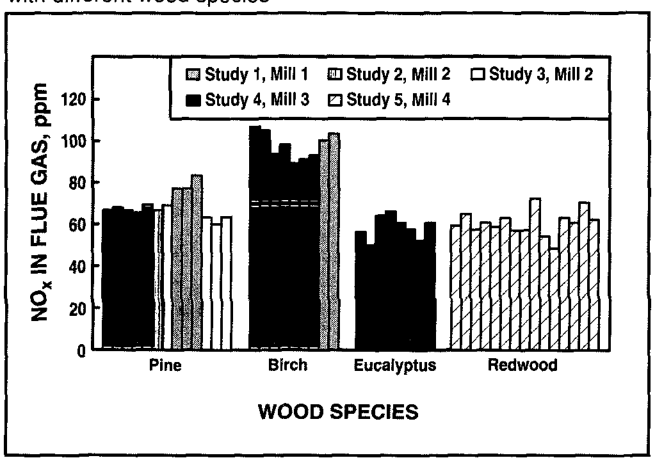
5. A schematic presentation of the behavior of the fuel nitrogen during black liquor pyrolysis



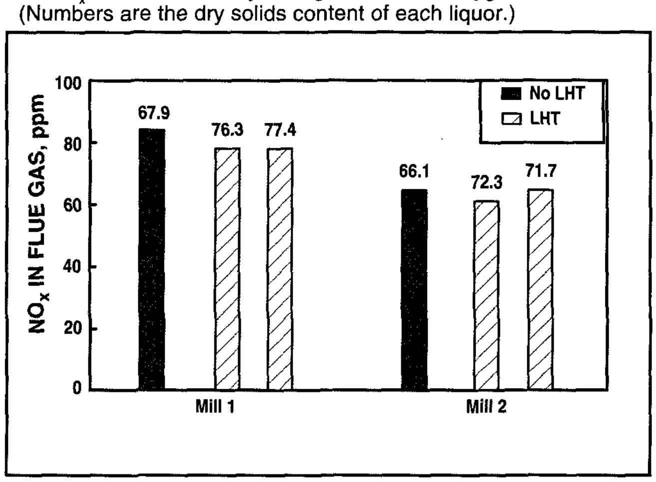
6. N_{fix}/N_{vol} release in black liquor pyrolysis



7. NO_x emissions in dry flue gases at 8% oxygen in different mills with different wood species



8. NO_x emissions in dry flue gases at 8% oxygen for two mills (Numbers are the dry solids content of each liquor.)



to the limited accuracy of the liquor nitrogen analysis method, however, this finding requires confirmation by a better technique.

Conversion of fuel nitrogen to NH_3 during pyrolysis was 7–28% and to NO it was 1–2%. NO released was independent of the nitrogen content of the liquor.

Low temperature devolatilization in muffle furnace

There were additional tests to determine the total nitrogen released during pyrolysis. In these tests, larger liquor samples underwent treatment in a muffle furnace at 400°C for 1 h. **Table III** shows the amounts of total volatiles as well as the nitrogen–, hydrogen–, and carbon–contents in the BLS both before the devolatilization test and in the char after the test.

There was no systematic variation in the amount of volatiles or nitrogen volatiles between different wood species except for the bagasse liquor.

On the basis of these tests, we can approximately estimate the main reaction routes of the fuel nitrogen during black liquor pyrolysis as **Fig. 5** depicts. About 20–60% of fuel nitrogen releases as volatile nitrogen compounds, N_{vol}. Approximately half of the N_{vol} is molecular nitrogen. The other half is mostly ammonia.

The amounts of volatiles are smaller for the heat–treated samples (3, 7, and 9) than for the original samples (2, 6, and 8). The difference between samples 2 and 3 is insignificant, however. The amounts of N_{vol} are considerably higher for the heat–treated samples than for the original samples.

The comparison of the total volatilized nitrogen, N_{vol}, calculated from these muffle furnace test results to N_{fix} released during single particle pyrolysis at 600°C (measured during the tube furnace test) is of interest. **Figure 6** shows the ratio of N_{fix}/N_{vol} for the sample pairs in their original and heat–treated states. Determination of the ratio in this figure used N_{fix} from the tube furnace test with an argon atmosphere and N_{vol} from the muffle furnace test with

III. Properties of liquor samples before and after 1 h pyrolysis in muffle furnace

Sample	*Description*	*Volatiles, % on dry solids*	*C, %*	*H, %*	*N, %*	*N-vol, %*[a]
1	Pine: orig.	-	40.9[b]	4.03	0.124 ± 0.025	-
	1 h 400°C	34.0	37.1[c]	1.33	0.155 ± 0.038	17.5
2	Birch: orig.	-	37.0	4.32	0.170 ± 0.010	-
	1 h 400°C	36.9	33.9	1.15	0.168 ± 0.024	37.6
3	Birch: orig.	-	36.3	4.21	0.166 ± 0.007	-
	LHT 1 h 400°C	36.8	33.1	1.10	0.154 ± 0.014	41.4
4	Pine: orig.	-	36.2	3.86	0.126 ± 0.007	-
	1 h 400°C	33.1	34.6	1.16	0.148 ± 0.020	21.4
5	Birch: orig.	-	33.6	3.65	0.150 ± 0.020	-
	1 h 400°C	32.8	30.8	1.05	0.178 ± 0.014	20.3
6	Mixed: orig.	-	33.3	3.75	0.141 ± 0.013	-
	1 h 400°C	28.2	31.6	1.59	0.160 ± 0.037	18.5
7	Mixed: orig.	-	33.3	3.63	0.140 ± 0.014	-
	LHT 1 h 400°C	27.0	30.7	1.36	0.142 ± 0.015	27.0
8	Pine: orig.	-	35.6	3.44	0.120 ± 0.009	-
	1 h 400°C	29.2	30.3	1.22	0.116 ± 0.019	31.6
9	Pine: orig.	-	37.7	2.66	0.106 ± 0.014	-
	LHT 1 h 400°C	24.3	28.8	0.95	0.083 ± 0.008	40.7
10	Bagasse: orig.	-	37.9	4.08	0.478 ± 0.028	-
	1 h 400°C	46.1	34.4	1.21	0.314 ± 0.024	64.6

[a] % of N in BLS
[b] % of BLS
[c] % of char residue

IV. Nitrogen content in the BLS

Sample	*Nitrogen, %*
Redwood liquor	0.08-0.10
Eucalyptus liquor	0.10
Pine liquor	0.10-0.19
Birch liquor	0.16-0.19

an air atmosphere. One should note that conditions of temperature and pyrolysis time were also different in the muffle furnace and the tube furnace. The muffle furnace tests used dry liquor samples. The tube furnace tests used liquors with dry solids contents of 50–72%. Consequently, the results in Fig. 6 are only preliminary.

Emission measurements in recovery boilers

Figure 7 shows recovery boiler NO_x emissions from different mills *(8)*. Although there are some variations for each mill, there is a clearly systematic difference between the various wood species. NO_x emissions are significantly higher for the birch liquor than for the other liquors. The eucalyptus and redwood liquors have the lowest NO_x emissions. **Table IV** shows the nitrogen contents in the BLS *(8)*.

The results suggest that the wood species used in pulping determine to a large extent the NO_x level in recovery boiler flue gases. Thus the liquor nitrogen content probably controls the NO_x level substantially. The furnace operation also influences the NO_x level, because the furnace operation controls the temperature distribution and the local air ratios in the various parts of the furnace.

Figure 8 shows NO_x levels in two mills in a period when LHT was in use and in a period without LHT. In both cases, NO_x emissions were at the same level or slightly lower with LHT than without LHT. The results indicate that LHT does not increase NO_x emissions in spite of the simultaneously increased dry solids levels.

The results of these mill studies are consistent with the assumption that N_{fix} released during pyrolysis may have an important role in formation of nitrogen oxide emissions in a recovery boiler.

Conclusions

A significant portion (20–60%) of the fuel nitrogen released during the black liquor pyrolysis. Roughly half of this is in fixed nitrogen species consisting primarily of ammonia. The remainder is molecular nitrogen.

The total amount of N_{fix} released during pyrolysis was almost linearly proportional to the liquor nitrogen content. The yield of N_{fix} for the birch liquors was significantly higher than for pine liquors. The yield of N_{fix} for the bagasse liquor was extremely high—almost an order of magnitude higher than for the other liquors.

Liquor preheating appears to decrease slightly the yield of N_{fix} during pyrolysis.

Fixed nitrogen species will readily oxidize to NO when the pyrolysis gases mix with air. If this conversion would be complete in a recovery furnace and this would be the only source for NO_x in a furnace, one would have NO_x emissions in the range of 31 ppm to 95 ppm (bagasse 460) at 8% oxygen with the ten liquors included in this laboratory study. This is very close to typical published values in boilers using these types of liquors.

NOx Emissions

A relationship between the pyrolysis yield of N_{fix} as measured in the laboratory and a NO_x emission from a full-scale boiler using the same liquor appears probable, although this does not directly follow from our data. Some support for this hypothesis comes from the NO_x measurements in full-scale boilers burning four different liquors. These measurements clearly indicate that one main variable in determining the NO_x level in a boiler is the liquor type. The boiler burning birch liquor gave significantly higher emissions than the three other liquors originating from pulping of pine, eucalyptus, and redwood. These liquors are not part of the ten studied here. The simple fuel nitrogen analysis values indicate, however, that the birch also had the highest nitrogen content of all four liquors.

The heat-treated liquors gave slightly lower NO_x emissions than burning of the same liquors without heat treatment.

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