"The Evolution of Fuel Nitrogen During Black Liquor Pyrolysis"

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Table of Contents

List of Tables

List of Figures

List of Figures (continued)

EXECUTIVE SUMMARY

The concern remains throughout industry high to obtain a better understanding of the formation of nitrogen oxides during black liquor combustion. The current understanding leaves us with the knowledge that NO_x is formed from the fuel nitrogen mechanism and thus is dependent on the nitrogen in the black liquor. Little information on the release of the black liquor nitrogen during the various stages of the combustion process is available. Therefore, a thesis was proposed to investigate the evolution of fuel nitrogen during black liquor pyrolysis.

During the past quarter, I have been in residence at Åbo Akademi University in Turku, Finland in the Combustion Chemistry Research Group (CCRG) where I am participating in a study to further investigate the nitrogen chemistry in black liquor combustion. This investigation, where Mikael Forssén is the principle investigator, is part of the LIEKKI Combustion Research Program of Finland which is directed by Professor Mikko Hupa. During the past four months, the project has been initiated. Therefore, most of the results presented in this report concern the equipment set up and the analyzer calibration work. However, the first set of nitrogen release experiments for black liquor droplet pyrolysis has been completed and those results are also presented briefly here and in greater detail in the report.

The nitrogen release observed during the pyrolysis experiments completed to date has indicated the greatest portion of the nitrogen to be released in the form of N_2. Char nitrogen analysis indicated about 50 % of the original black liquor nitrogen to be released during pyrolysis at 800 °C in an N_2 carrier gas. The gas phase measurements showed that about 18 % of the released nitrogen was in the form of NO. Very little NH_3 was observed in the gas phase. Therefore, approximately 78 % of the released nitrogen was likely N_2. It was also observed that the nitrogen release as NO and NH_3 increased with increasing pyrolysis temperature.

INTRODUCTION

The formation of NO_x during the combustion of black liquor remains of interest in the chemical recovery process and to boiler manufacturers. Information on the generation of NO_x during the various stages of black liquor combustion is limited. However, the general belief is for NO_x to be created *via* the fuel-N mechanism. Here, the nitrogen in the fuel can be released to form NO directly, to form intermediate species such as HCN and NH_3 which can react further creating N_2 or NO based on the available oxygen, or to form N_2 directly.

The importance of each of these fuel-N pathways to the overall formation of NO during black liquor pyrolysis and char burning is of current interest. The first investigation of these pathways was reported by Aho, *et. al.*[1] Black liquor droplet pyrolysis indicated approximately 20-60 % of the original fuel nitrogen to be released. The primary nitrogen compound observed in the initial pyrolytic gases was NH_3. Only small portions of the fuel nitrogen which was released were observed as N_2 or NO. Measurements were also made for the HCN intermediate species; however, very little or none was detected.

The total fixed nitrogen (N_{fix}), the sum of NO plus NH_3, was 10-30 % of the total fuel nitrogen content. The rate of the release of fixed nitrogen was reported to increase with increased pyrolysis temperature. Also, the yield of the fixed nitrogen was found to be liquor dependent as well as proportional to the initial amount of nitrogen in the fuel. Finally, the conversion of the fuel nitrogen to fixed nitrogen also increased with increasing fuel nitrogen content.

Aho's study provided the intitial knowledge of the fuel nitrogen pathway to NO during black liquor pyrolysis. As such, this knowledge must be verified and expanded to continue to understand the formation of NO during black liquor combustion. In this report, initial efforts to repeat Aho's pyrolysis experiments are described. The overall objective of these experiments

was to measure the nitrogen release as NH_3 and NO during the pyrolysis of several black liquors in the temperature range from 300-1000 °C. An ultimate char analysis for total remaining nitrogen was also desired to bring closure to the nitrogen balance for the experiments. The results of these experiments are presented and discussed using Aho's results as a basis for comparison.

EXPERIMENTAL

The experimental section is divided into two parts. The first concerns the calibration work for the NO analyzers and includes the equipment set up. The second part decribes the pyrolysis experiments. Results and discussion for both parts follows immediately at the end of each.

Part I. NO Analyzer Calibration

The experimental system was arranged so that the nitrogen gases released during the pyrolysis of black liquor droplets could be measured. The NO released directly and that formed from NH_3 was measured simultaneously using two NO analyzers. The first portion of the experimental work involved setting up the equipment and calibrating the analyzers. Confidence in the analyzer performance is necessary to have confidence in the experimental findings. Thus, much work was done to set up the analyzers and to monitor their performance. Details of this work are presented in the following sections.

Equipment Description and Experimental Set Up

The general set up for the fixed nitrogen gas measurements includes a quartz reactor, a tube furnace (Carbolite Furnace Limited), the NO analyzers (Advanced Pollution Instrumentation, Inc.), a thermal oxidizer (Measurement Technologies), and a CO_2 analyzer

(Hartmann and Braun). A block diagram of the experimental arrangement is given in Figure 1. For the calibration of the analyzers, certified gases, NO and NH_3, were directed from the gas cylinders through calibrated rotameters into the reactor in the tube furnace. The gases were then directed out of the furnace by the N_2 carrier gas where the flow was divided so that the desired flow rates were taken into each of the analyzers for concentration measurements. The data from the experimental work, as well as from calibration, was acquired using computer data aquisition. The CO_2 analyzer was set up in parallel with both of the NO analyzers.

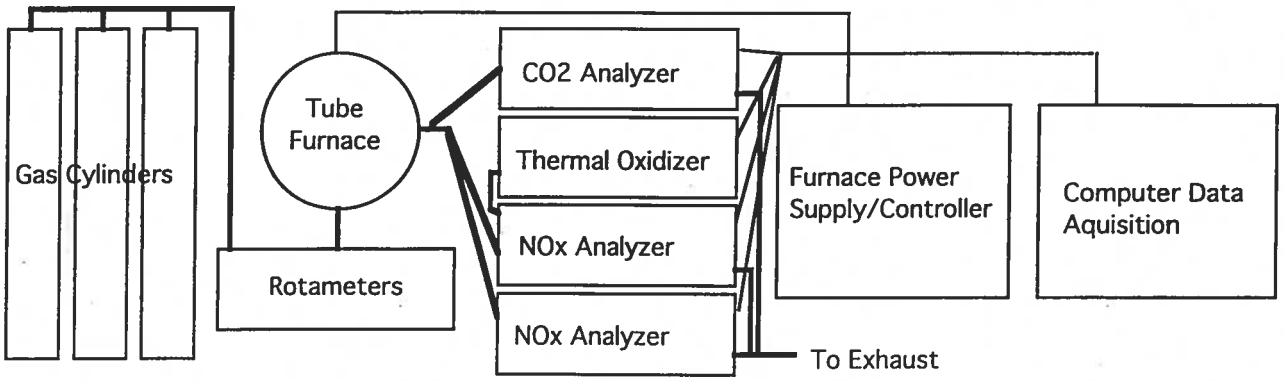

Figure 1. Experimental block diagram for the measurement of nitrogen released during black liquor pyrolysis.

The quartz reactor is illustrated in Figure 2. During analyzer calibration, all gases were sent through the reactor so that the measurements would have a similar response time as during experimentation. The reactor was air tight during calibration work. The quartz components of the reactor have ground glass joints and the droplet insertion rod was in the down position which closed the top of the reactor with a teflon tape plug. The gas lines to and from the analyzer are teflon and Swaglock connecting joints were used on the gas lines.

During calibration, the certified gases, either NO or NH_3, were fed individually into a t-joint which split the flow so that it entered the reactor on opposing sides. When both of the calibration gases were fed, the gases were combined with a t-joint and then split after about 5 cm

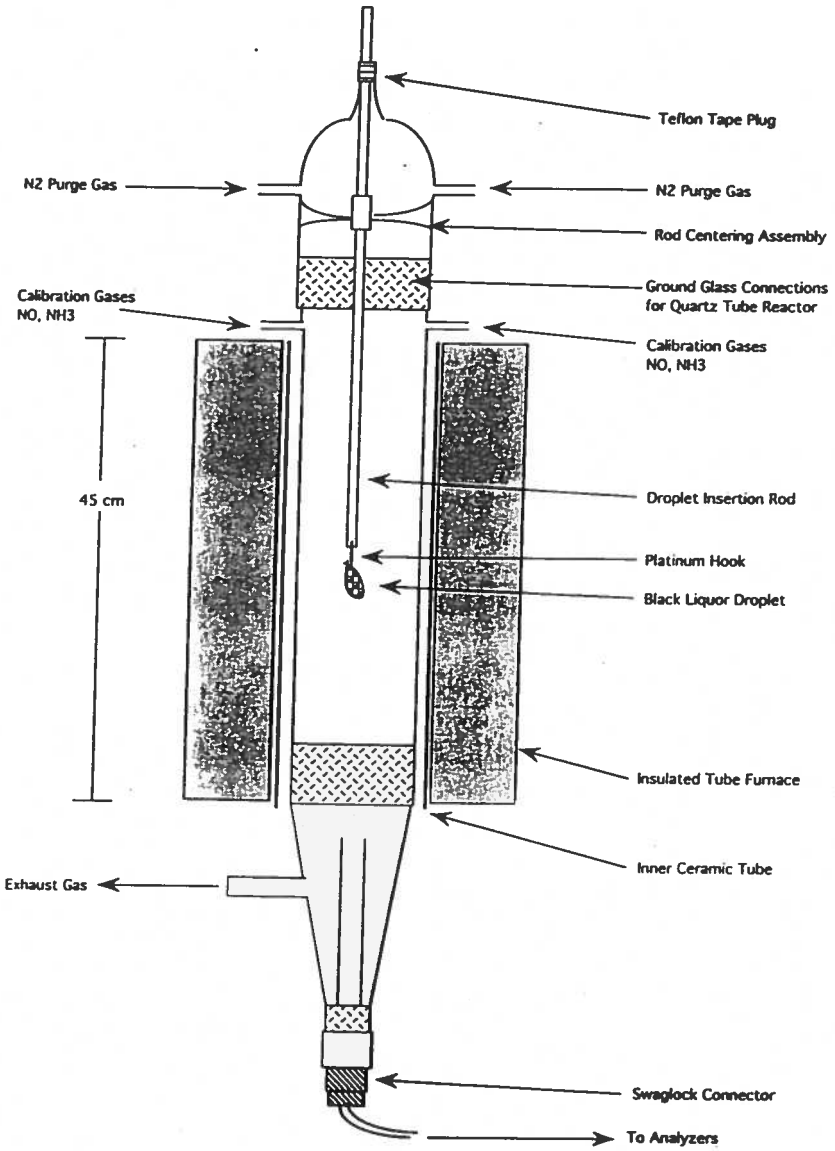

Figure 2. Quartz tube reactor, Åbo Akademi, CCRG, used for the pyrolysis of black liquor droplets.

by another t-joint which allowed the flow to enter the reactor on opposing sides. The N_2 carrier gas flow was split by a t-joint and entered the reactor, again on opposing sides, about 17 cm above the entrance of the calibration gases. The gases travelled the length of the reactor (approximately 52 cm) where they exited. Approximately 50 l/h went to the CO_2 analyzer, 33 l/h went to the analyzers, and the remainder was exhausted. The NO analyzer stream was

brought to a total of approximately 53 l/h with air to provide for an 8 % oxygen concentration. All gas flows were measured and controlled with calibrated rotameters. Both the N_2 carrier gas and the air were dry. A moisture trap of silica gel was used in the gas lines to further assure the gases were dry. The total gas flow into the reactor throughout the calibration work was 300 l/h and therefore, all gas flows were in the laminar regime. (See the Appendix for the calculation). The flow rates and pathways are more clearly identified in Figure 3.

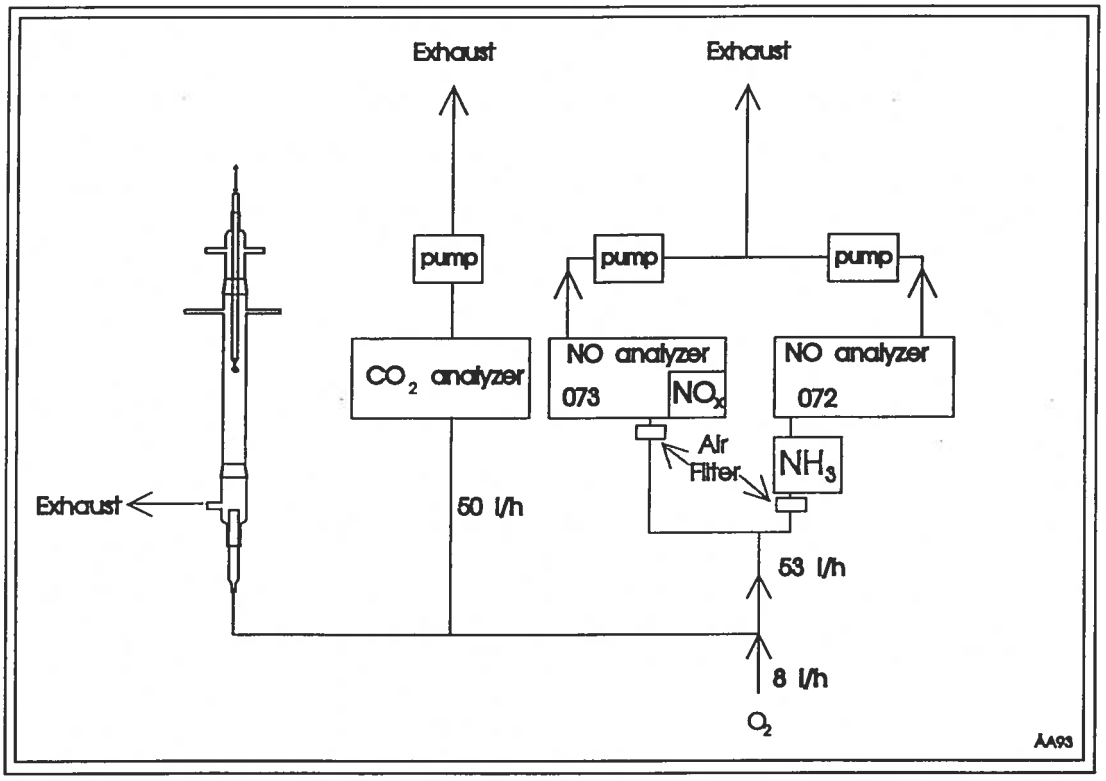

Figure 3. Nitrogen release measurement experimental set up specifying approximate flow rates.

The "Zero" gas for the calibration measurements consisted of the carrier gas at the specified flow rate and was diluted with air to 8 % oxygen going to the analyzers. In this way, the analyzers measured the zero value to be the carrier and dilution gases. For the zero gas measurements, the t-joint was closed such that only the nitrogen carrier gas entered the top of the reactor.

The CO_2 analyzer was an NDIR-industrial photometer and was used during calibration to monitor the system for air leaks. The gas flow to the NO analyzer was split with a Swaglock joint so that half of the flow went to one analyzer, designated as 072, and half the flow went to the other analzyer, designated as 073. The 072 analyzer was set up such that the calibration gas sample entered the NO analyzer and then could be sent to a thermal oxidizer to convert the NH_3 to NO or could be analyzed for NO directly. The converter pathway was used throughout the calibration and the experimental work. The gases exited the converter and again entered the analyzer for detection of the total NO (*i.e.* the original NO plus the NO from the conversion of the NH_3). The NH_3 was converted in the thermal oxidizer simply by high temperature (920 °C) oxidation where the hydrogen was stripped from the NH_3 forming water and the nitrogen was then oxidized to NO.

The 073 analyzer had an internal converter which could be switched on to allow for measurement of the NO_2 gases. The NO_2 converter used a molybdenum catalyst to reduce the NO_2 to NO which could then be measured in the NO analyzer. However, the converter was not used during either the calibration or experimental measurements as its formation was found to be negligible. The NO analyzers used the principle of chemiluminesce detection for the NO measurement. An ozone generator and a vacuum pump were included with each of the analyzers. Each of the NO analyzers, also, had an air filter at the sample entrance for fume capture.

Each of the analyzers was set up to function at three concentration ranges to maximize the sensitivity of the measurements. The 072 analyzer had range 1 (R1) for detection of gases at 0-10 ppm NO, range 2 (R2) for 0-60 ppm NO, and range 3 (R3) for 0-200 ppm NO. The 073 analyzer was set up with range 1 (R1) for gases at the 0-3 ppm NO level, range 2 (R2) for gases at 0-15 ppm NO, and range 3 (R3) for gases at 0-60 ppm NO.

Thermal Oxidizer Optimization

Optimization of the thermal oxidizer was required to maximize the conversion of the NH_3 to NO. The optimization involved identifying the appropriate internal oxidation tube oven temperature and the appropriate oxygen level to be used with the gas sample stream. The temperature optimization was done by evaluating the conversion of NH_3 to NO at various concentrations and between temperatures of 900-1050 °C at 25 °C intervals. A certified gas at 234 ppm NH_3 in He was fed to the reactor and thus to the converter at concentrations of 30 ppm NH_3 and 5 ppm NH_3 in the total flow with 8 % oxygen in the sample stream. The concentration of the NH_3 was verified by ISE and FT-IR measurements.

The conversion improved with the increased temperature from about 41 % to nearly 100 % with 30 ppm NH_3. At 5 ppm NH_3, the conversion also improved with increased temperature from 54 % to about 76 %. However, no clear optimum was observed at any one temperature for both concentrations for the conversion of NH_3. It was noted, though, in further tests that the conversion was much higher at all temperatures for very low NH_3 concentrations. After considerable deliberation, the thermal oxidizer temperature set point was defined to be 920 °C based on the manufacturer's recommendation.

The effect of oxygen content in the gas sample stream on the conversion of NH_3 to NO was also tested. Oxygen concentrations of 1 to 8 % in air were used with 10 and 30 ppm NH_3 to monitor the effects of oxygen on the NH_3 conversion to NO. The conversion steadily increased with increasing oxygen concentration. This is shown schematically in Figure 4. Thus, a level of 8 % oxygen was then defined as the optimum oxygen level to be used throughout the calibration and pyrolysis experiments.

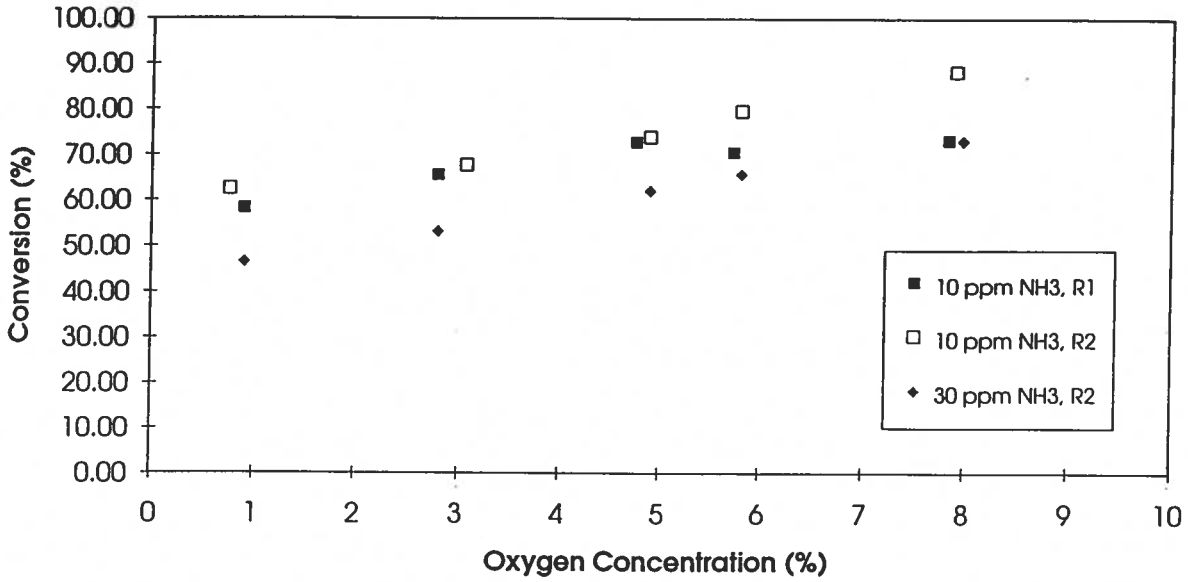

Figure 4. Effect of oxygen concentration on the conversion of NH3 to NO in the thermal oxidizer. NH3 concentrations of 10 and 30 ppm measured as NO by 072 analyzer at ranges 1 (R1) and 2 (R2), as indicated.

NO Analyzer Calibration

Prior to calibration of the analyzers, the zero and span point for the analyzers had to be set. For the zero point, a zero gas of nitrogen was fed to the reactor at 300 l/h and the sample stream to the analyzers was diluted in the same manner as that which would occur during calibration and experimentation. The system was allowed to stabilize and then the analyzer was adjusted such that the measured response was zero. For the span point adjustment, a calibration gas at 80 % of R3 for each of the analyzers was fed to the system. When a stable measurement was observed, the analyzer was adjusted such that the measured response was likewise 80 % of the full scale. The full scale response for all ranges was 5.0 volts and as such the sensitivity of the measurements remained high at all ranges for each of the analyzers.

The NO analyzers were calibrated individually by feeding known concentrations of certified calibration gas (195 ppm NO in N_2) to the reactor and thus to the analyzers for measurement. Five concentrations of NO were delivered to the reactor at 80, 60, 40, 20, and 10

% of the full scale range of measurement for each analyzer. The concentration set points were determined based on the analyzer reaction cell concentrations. Thus, the air dilution was also taken into account in this way. For example, for the 072 analyzer at R3, concentrations of 160, 120, 80, 40 and 20 ppm NO were fed to the reactor in a total volumetric flow of 300 l/h. The NO flow rates were calculated and delivered to the reactor *via* the calibrated rotameters. The balance of the flow was calculated for the N_2 carrier gas. All calibration measurements were made at room temperature.

At each concentration within each range, the system was allowed to stabilize and then the analyzer voltage response was recorded. The linear relationship was calculated between the values of slope (m) and the intercept (b) for the true concentrations (x) and the measured response (y). The regression analysis was done on EXCEL. The calibration curves were "forced" through zero by including the (0,0) point in the regression analysis. This allowed for more accurate determination of the concentrations in the lower portion of each range. The equation for the calibration curve and the corresponding correlation coefficient was obtained directly from the regression analysis.

Likewise, the NH_3 calibration gas was fed to the reactor at several concentrations for each of the R1 and R2 072 ranges. At the lower concentrations, a second NH_3 certified calibration gas, whose concentration was 47.5 ppm NH_3 in He, was used. The analyzer voltage response was taken and used to calculate the regression line in the same manner as for the NO gases.

The analyzers were monitored daily for stability and accuracy of the NO and NH_3 measurements by feeding known concentrations of the gases individually and in combination with each other. Because of the possibility for NO-NH_3 reactions at higher gas concentrations, the concentrations of NO and NH_3 were always 10 ppm or less. The NO and NH_3 were fed individually to the system at concentrations of approximately 1.5, 2, and 4 ppm and 1.5, 5, and

10 ppm, respectively. Also, NH_3 at about 2, 3, and 5 ppm was fed to the reactor in combination with NO at 1, 1.5, 4, and 6 ppm. For each test, the system was allowed to stabilize and the voltage response was taken. The appropriate calibration equation was then used to determine the measured concentration.

Because of the low conversion of NH_3 from the thermal oxidizer, the concentration of the NH_3 during the measurements had to be calculated in two ways depending on the system. If the NH_3 was the only gas fed to the system, then the NH_3 calibration equation could be used directly. However, when both the NO and NH_3 were fed to the analyzers, the NH_3 concentration had to be determined by a series of calculations. First, the difference in the NO measurements between the two analyzers had to be determined. This provided the concentration of NO that must have been formed by the conversion of the NH_3. Second, the NO calculated by the difference was substituted into the 072 NO calibration equation to determine the corresponding voltage response. This voltage respresented the portion of the total NO that was formed from the conversion of NH_3. Finally, this voltage could be used with the 072 NH_3 calibration equation to determine the original concentration of the NH_3.

The relative error in the response was determined by subtracting the true values from the measured values. The averages for each set of tests (where n = 3 when the gases were fed individually and n = 12 when the gases were fed in combination) were determined and used as a basis to monitor the instruments' performance. Based on the analyzer response over a period of time and the known accuracy of rotameter controlled flows, a 10 % margin of error in the average measurements was determined to be the limit for recalibration. The stability of the instruments came to a level where only weekly calibration was required. During the pyrolysis experiments, the system was calibrated three times: once initially and twice during the actual experimentation time period.

Results and Discussion

The calibration curves throughout the set up and the experimental work indicated very good linearity. The calibration curves for the 072 analyzer provides an example of the linearity and is illustrated in Figure 5. Since the system was set up to operate in the lower concentration ranges, the 072 R2 and R3 ranges were not used in these experiments. Likewise, the 073 R3 range was not used. The use of only the lower concentration ranges was verified initally by burning several black liquor droplets to observe the level of nitrogen release. All concentrations were observed to be 3 ppm NO or less even at conditions for maximum nitrogen release. The correlation coefficients were on average 0.999 (± 0.0005) for the 072 R1 NO calibration equation, 0.999 (± 0.0003) for the 073 R2 NO calibration equation, 0.988 (± 0.006) for the 073 R1 NO calibration equation, and 0.996 (± 0.002) for the 072 R1 NH_3 calibration equation.

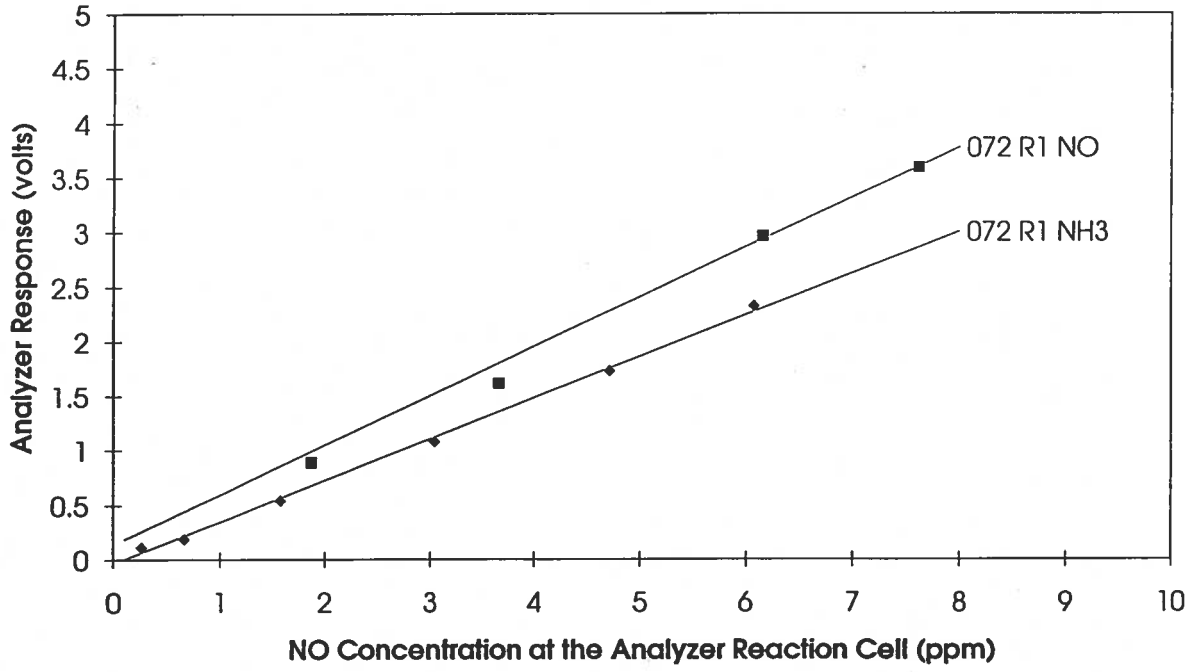

Figure 5. Calibration curves for NO and NH3 concentration measurements made with the 072 analyzer at R1.

The differences were minor in the calibration equations for a given range when recalibration was required. Only small changes in the slope of the calibration equation were

observed as can be seen in Figure 6. Here, the curves are shown for the three separate NO calibrations which were made for the 072 analyzer during the pyrolysis experimentation. Similar small changes in the slope were observed for the NH_3 calibration curves as well as for the other analyzer.

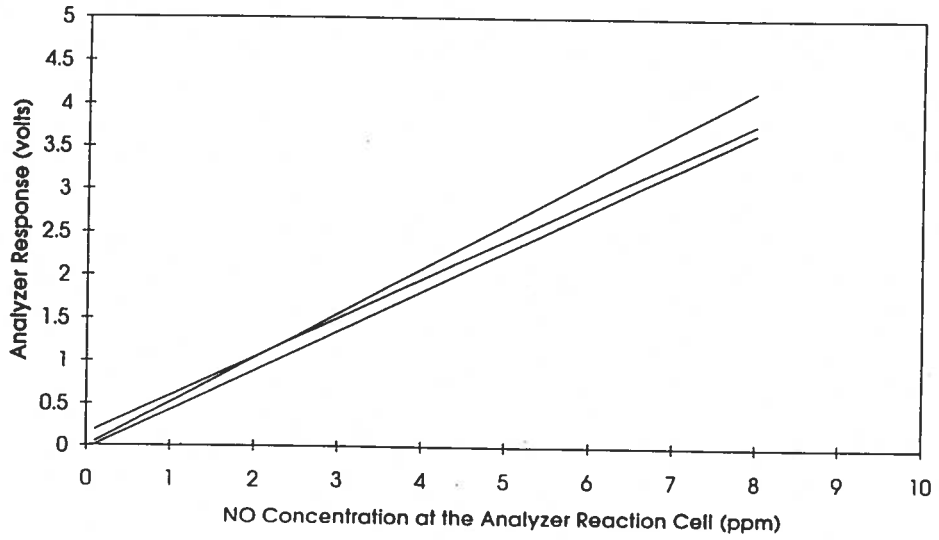

Figure 6. Curves for three different calibrations for NO concentration measurements made with the 072 analyzer at R1 illustrate the slight change in slope and the stability of the analyzers.

The outcome of daily monitoring of the analyzers confirmed their stability as well as their ability to make accurate measurements for the unknown NO and NH_3 gas concentrations during experimentation. The values for the monitoring tests, described in the previous section, are indicated in Table 1. The first column provides the number of days of testing chronologically; however, they are not consecutive. The second column indicates the average percent difference in the calculated and the true concentrations of NO as determined by the corresponding calibration curve. Similar averages were determined for the values presented in the third through fifth columns. The average was determined from three data points when only one of the calibration gases was fed, while the average was determined from 12 data points when both gases were fed to the system.

Table 1. Results of daily monitoring of the NO analyzers' calibration stability.

Day	072 Ave. % Dif. NO (Calculated -True) only NO used	073 Ave. % Dif. NO (Calculated -True) only NO used	072 Ave. % Dif. NH_3 (Calculated -True) only NH_3 used	073 Ave. % Dif. NO (Calculated -True) NO and NH_3 used
1*	0.41	0.13	0.03	0.00
2	-1.99	-2.09	0.73	-1.31
3	2.67	0.36	-0.10	-3.79
4	-6.40	-9.02	-6.86	-4.84
5	2.31	-0.42	5.23	-1.17
6	9.34	1.54	8.35	4.59
7*	7.89	6.15	6.40	5.65
8	4.49	-0.20	13.37	7.08
9	9.35	4.01	33.15	8.13
10*	3.08	-0.20	-3.96	-1.94
11	8.60	-3.02	-2.27	-1.72
12	7.00	-1.34	-3.34	-2.01

*Indicates day of recalibration.

The values were found to be both higher and lower than the true values indicating no systematic error or bias in the measurements. Nearly all observed values were less than the set limit of 10 % error. The error for any single measurement, however, did extend from about -14 % to 16 % for the NO measured by the 073 analyzer, from about -11 % to 18 % for NO measured with 072, and from -16 % to 20 % for NH_3 measured by 072. In the most extreme case, the average percent difference was about 33 % for the NH_3 measured by 072. At this point, the calibration was redone.

The problem of the low conversion of NH_3 to NO was not entirely corrected and became more evident when both the NO and NH_3 were fed to the reactor for concentration measurements. Throughout the testing described above, the NH_3 concentration determined from its conversion to NO was consistently low. The average percent differences were in the range of -8 % to -24 % for the calculated and true NH_3 concentrations from the twelve measurements

made when both NO and NH_3 were fed to the system. Only in one test was the average percent difference greater than zero. Here, the average was 0.11 %. However, it was noted that at very low concentrations, the accuracy of the measurements greatly improved. This is indicated in Figure 7 where data is plotted from several days during the experimental period. When the delivered NO concentration was less than about 4 ppm and that of the NH_3 was only about 3 ppm, the calculated conversion of NH_3 to NO ranged from a low of 84.3 % to a high of 107.7 %. The average percent conversion was 96.8 %.

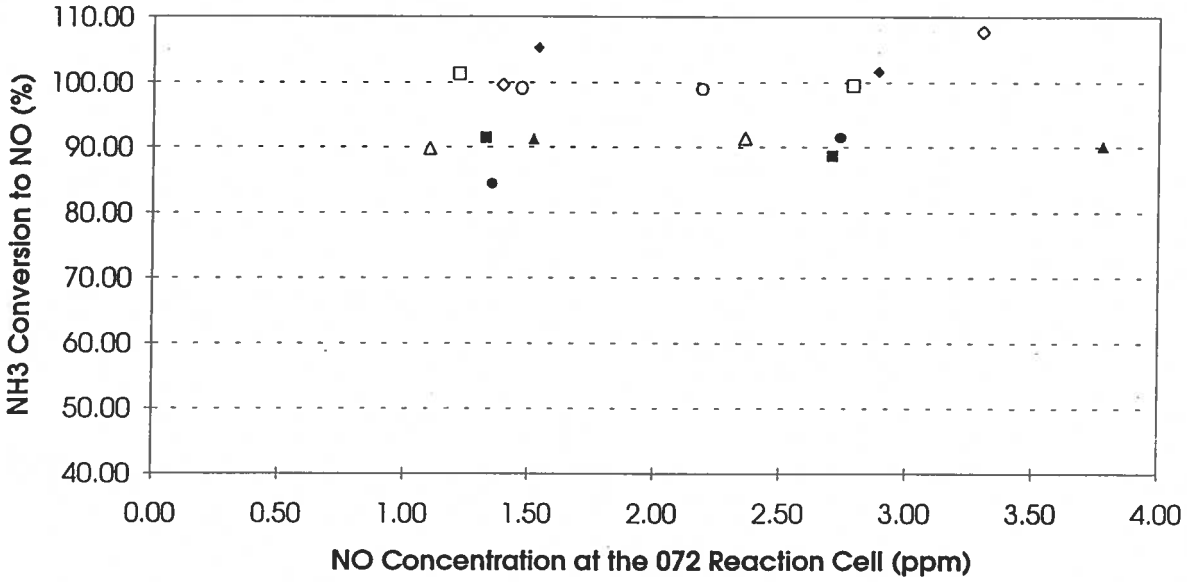

Figure 7. Conversion of NH_3 to NO for the gases delivered together to the reactor. The average conversion was found to be 96.8 % at concentrations of < 4 ppm NO and ≤ 3 ppm NH_3.

A high total flow rate for the pyrolysis experiments was used to maintain the concentrations of the nitrogen species in the gases at very low levels. In this way, the accuracy of the measurements was assured to be within the 10 % margin that had been established. The results of the calibration work indicated that the analyzers could maintain the stability and accuracy for measurements of unknown NO and NH_3 gas concentrations during the black liquor pyrolysis experiments.

Part II. Black Liquor Droplet Pyrolysis Experiments

The second part of the experimental work involved the black liquor droplet pyrolysis experiments which were done in a similar fashion as Aho's reported experiments.[1] The details of the experimental work are first presented and then are followed by a results section with a discussion comparing this work to Aho's.

Liquor Description

Four kraft black liquors were used in the experimental work. These liquors were obtained at a high solids level from separate mills approximately six months prior to the starting date of the pyrolysis experiments. Liquor 1 was from pine, liquor 2 was from a pine/birch mix (approximately at a 45:55 ratio), liquor 3 was from eucalyptus, and liquor 4 was from southern pine. The average dry solids levels for the liquors were 71.2, 74.8, 67.6, and 72.7 %, respectively, for the four liquors. Solids levels were measured in triplicate at Åbo Akademi, CCRG based on the TAPPI standard method. The results of the elemental analysis and the analysis of the inorganic composition are given in Tables 2 and 3, respectively. Elemental analysis as well as the inorganic composition was done at KCL (Central Laboratories of Finland). All of the liquors were stored as samples of approximately 100 ml in air tight containers at 4 °C. The heating values (calorimetric) for the four liquors were 14.7, 13.86, 14.65, and 13.93 MJ/kg, respectively, on a dry solids basis.

Table 2. Elemental analysis of kraft black liquors (reported as % of dry solids).

Element	Liquor 1	Liquor 2	Liquor 3	Liquor 4
C	35.8	33.1	37.3	34.3
H	3.6	3.4	3.6	3.4
N	0.06	0.07	0.09	0.06
Na	21	25.9	19	19.7
K	1.8	1.8	1.8	3
S	4.6	5	3.4	5.2
Cl	0.5	0.6	1.6	0.9
O*	32.6	30.1	33.2	33.4

*Calculated by difference.

Table 3. Composition of inorganic sodium salts of kraft black liquors (reported as % of dry solids).

Element	Liquor 1	Liquor 2	Liquor 3	Liquor 4
Na_2SO_4	2.4	3.4	1.7	5.4
Na_2CO_3	8.4	10.4	9.3	16.9
Na_2SO_3	0.7	0.6	0.2	0.8
NaOH	1.7	0.1	--*	1.9
Na_2S	6.3	7.5	4	5.6

*No observation made. The effective alkali as NaOH, however, was reported as 1.4 %.

Pyrolysis Procedures

Individual black liquor droplets were made for the pyrolysis experiments. Black liquor was transferred from the storage container to a hook with a spatula to make the droplet. The target droplet weight was 15-25 mg; however, the weight of droplets used in the experiments ranged from about 9 to 32 mg. Each droplet was carefully weighed and allowed to dry in air for a minimum of 15 minutes and then in the nitrogen purge for three to five minutes prior to being pyrolyzed. A weight loss of 5-10 % (*i.e.* 1-2 mg) was observed during the "drying" period. The droplet surface was considered dry prior to pyrolysis.

The hook with the droplet was transferred to the insertion rod hook to be pyrolyzed. The purge drying occurred with the insertion rod in the up position allowing the nitrogen to flow over the droplet and through the reactor. The data acquisition was started at the end of the purge drying. The droplet was manually inserted to the pyrolysis position approximately 30 cm into the furnace. A lag time of 7-12 seconds was noted between the start of data acquisition until the droplet was in place. The gas flow through the system to the analyzers had a residence time of about 10 seconds for the 072 analyzer and 9 seconds for the 073 analyzer, which was measured at 300 l/h N_2 at room temperature.

Data was collected throughout the 300 seconds for the droplet pyrolysis at the indicated temperatures from 300-1000 °C. Liquors 1 and 3 were pyrolyzed at 100 °C intervals while liquors 2 and 4 were pyrolyzed at 200 °C intervals. The remaining char was lifted to the up position and allowed to cool in the nitrogen purge for 2-3 minutes above the furnace. Further cooling in the nitrogen purge was done by removing the top of the reactor to the lab bench. The total cooling time in the purge was a minimum of five minutes; however, much longer times were required at the higher temperatures to assure the char did not gasify in the air. The cooled char was weighed and retained for nitrogen analysis.

The pyrolysis tests at a given temperature were done in random order to eliminate the possibility of instrument drift affecting the results. A total of seven replicates were done at each temperature as indicated. The chars for all replicates were combined and submitted for total nitrogen determination by the Antek method. These analyses were made at EMPA (Swiss Federal Laboratories for Materials Testing). The char samples were ground prior to analysis and the reported values are the average of three replicates.

Data Analysis Procedures

All data was taken directly during pyrolysis by a data acquisition system. The program was set up to collect data at 0.1 second intervals for a total of 300 seconds. However, only data at one second intervals was used in the analysis. This was done to reduce the computer calculation time and for ease of data handling. The data files for each droplet were treated individually and then the resulting data from the seven replicates was combined to get an average pyrolytic volatiles yield as well as the average nitrogen release as NO and NH_3. The raw data for the nitrogen release was collected as a voltage response from the analyzers. This response was then substituted into the appropriate calibration equation to get the total NO measured at the reaction cell by each analyzer. A positive difference in the 072 minus 073 total NO concentration was used to calculate the voltage responsible for the NO produced from the

NH_3 in the system. This voltage response was then used to calculate the original NH_3 released during the pyrolysis. In this way, the low coversion of the NH_3 to NO could be accounted for.

The appropriate corrections in the NO and NH_3 concentrations were made for the air dilution and for the carrier gas. The corrected concentrations were then integrated for the entire 300 second pyrolysis time to obtain the total concentration for the nitrogen released during a given pyrolysis run. The 300 second integration interval was chosen so that the data at all temperatures could be treated in the same manner. The results are presented in the following section.

Results and Discussion

In general, the pyrolytic volatiles yield of the liquors was similar throughout the temperature tested and the averages are indicated in Figure 8. The standard deviations calculated for the replicates of these measurements were very low as shown by the error bars in the figure. This indicated a high degree of reproducibility for the measurements. A noticeable increase in the weight loss of approximately 30 % was observed between 800 and 900 °C for all liquors. It was also noted at the lower temperatures, from 300-500 °C, that little to no fuming was visibly observed and the degree of swelling for the particles was small but increasing with temperature. It was estimated from char particle observations that maximum swelling occured at 800 °C. At 600-1000 °C, the deposition of fume was noted on the lower portion of the quartz reactor.

Examples of the nitrogen release profile at each temperature is given in Figure 9 for liquor 1. The concentrations presented in these plots have not been corrected for dilutions. At the lowest temperatures, the level of nitrogen release was very small and was hardly detected by the analyzers. It was taken that the pyrolysis stage of black liquor combustion was not yet completed at the end of the 300 second pyrolysis period at the lowest temperatures. At slightly higher temperatures, the nitrogen release was slow by comparison to the upper temperatures and

lower amounts of the nitrogen were released. The NO profiles shown in Figure 9 only show single peaks for the nitrogen release, whereas multiple peaks were observed in Aho's work[1] for the NH_3 species. Likely, the residence time of the gases was shorter for Aho's study and the analyzers had a quicker response.

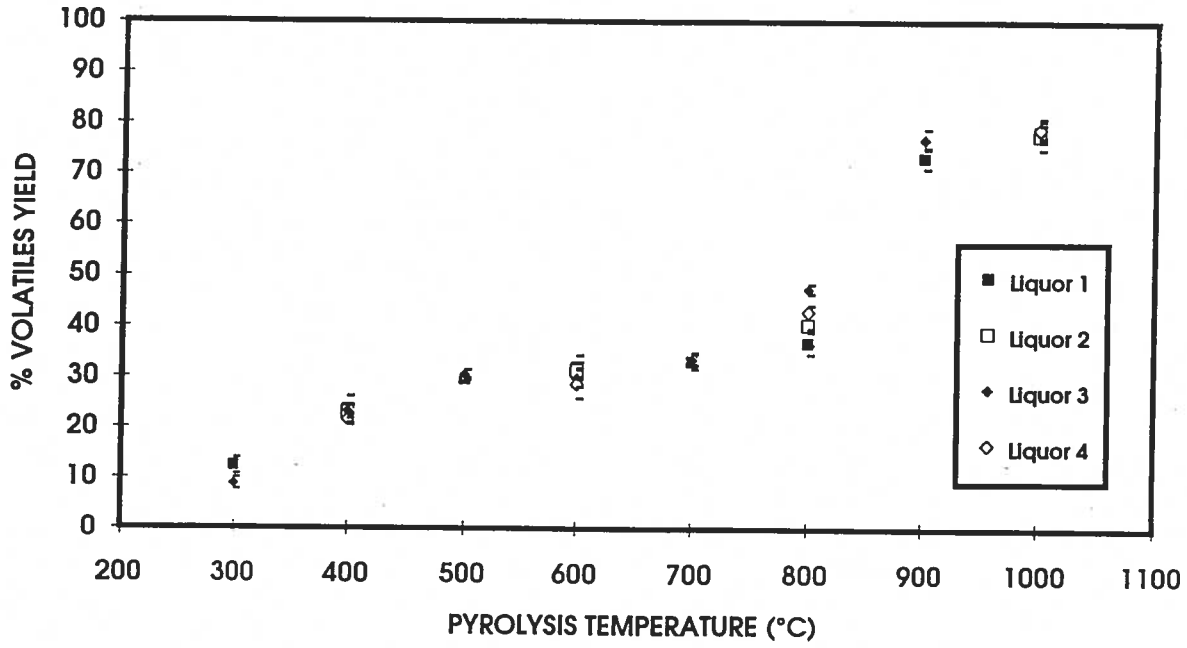

Figure 8. Pyrolytic volatiles yield (expressed on a dry basis) for liquors at temperatures from 300-1000 °C in N_2.

The nitrogen release as NO was fastest at 700 °C for liquor 1 as is indicated by the maximum height of the peak. However, the maximum amount of NO was observed at 600 °C for this liquor, while the maximum amount of N_{fix} was observed at 900 °C. The total fixed nitrogen, defined as $N_{fix} = NO + NH_3$, during pyrolysis for each liquor is shown in Figure 10, while the NO and NH_3 split for the liquors is indicated in Figure 11. The N_{fix} release is presented as the percent of the total liquor nitrogen and in nearly all cases, it was observed to be less than or equal to 10 % of the original liquor nitrogen. An increase in the N_{fix} release with an increase in the pyrolytic temperature was observed with all liquors.

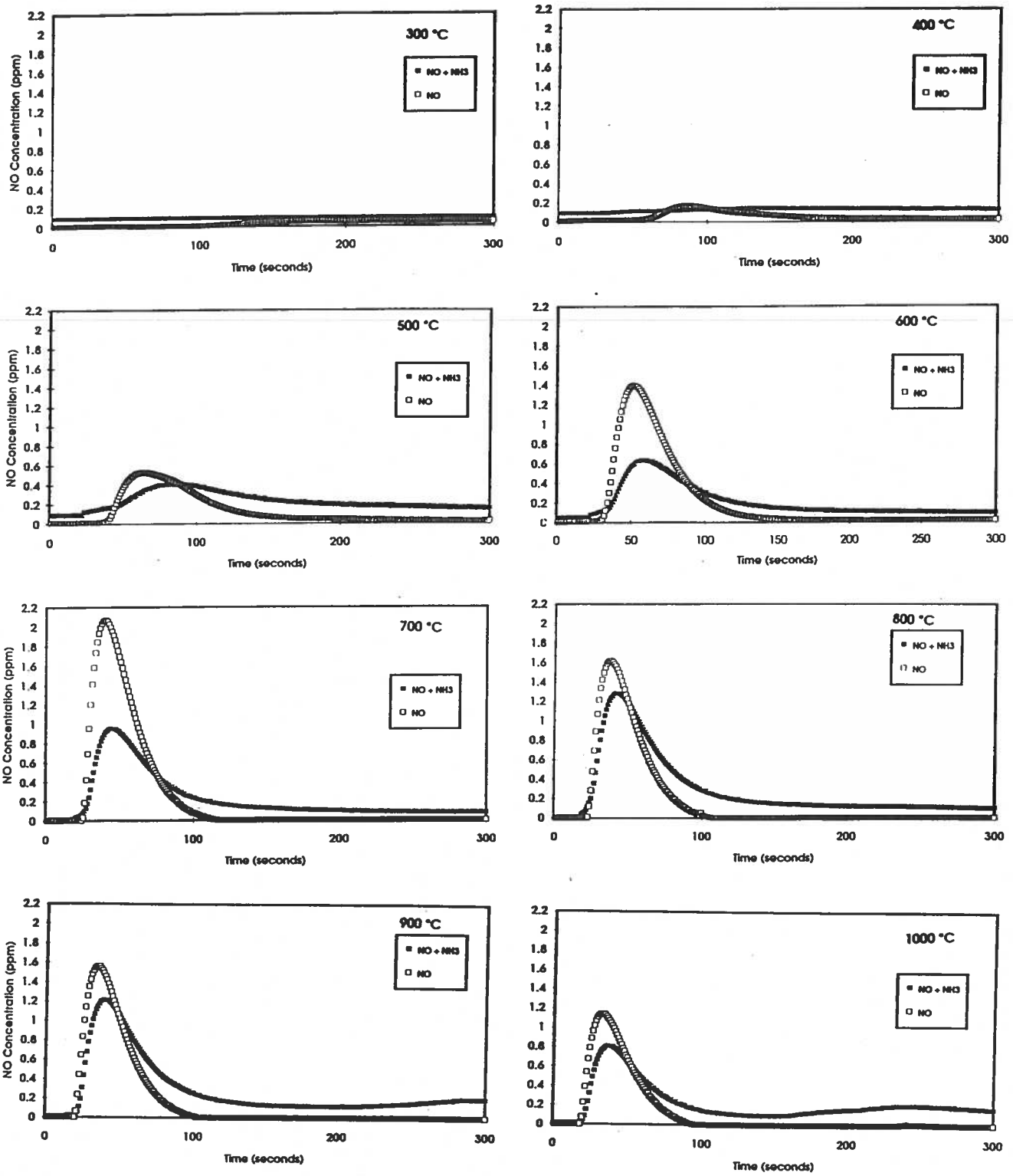

Figure 9. Liquor 1 nitrogen release for 20 mg average droplets at temperatures from 300-1000 °C. Note that the NO concentration has not been corrected for dilutions.

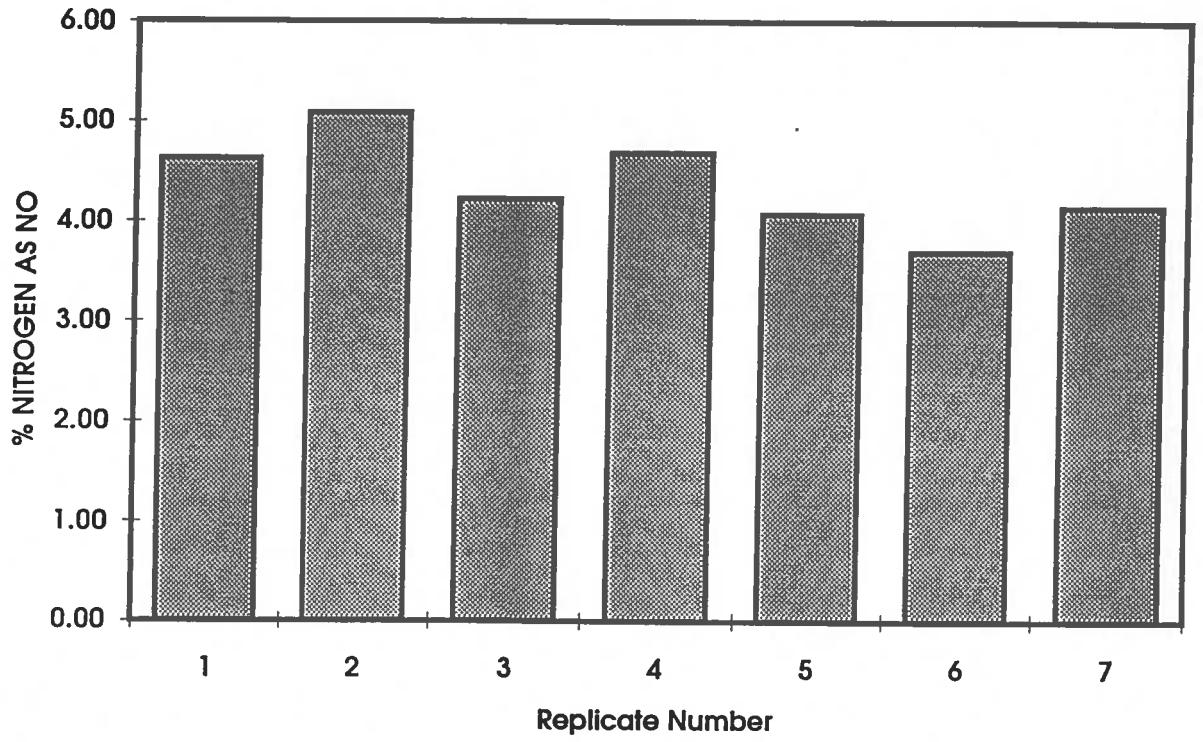

Figure 12. Reproducibility of nitrogen released as NO for Liquor 3 at 900 °C. The standard deviation for the measurements is 0.46.

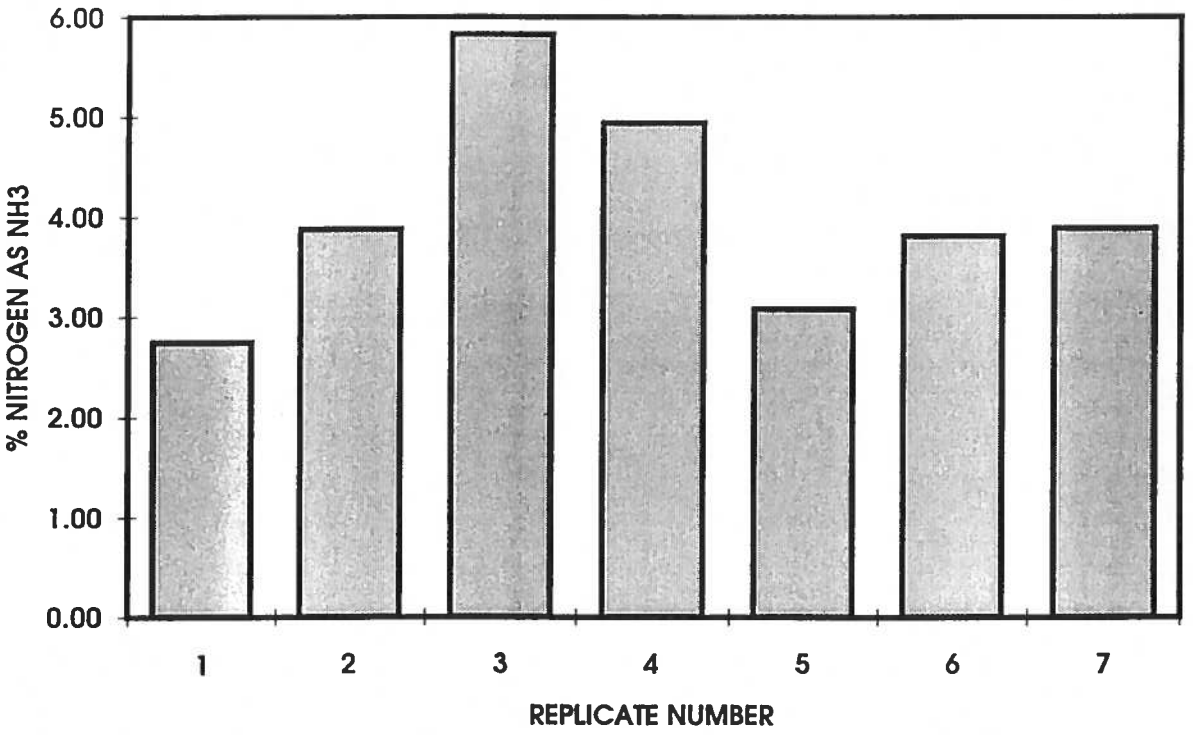

Figure 13. Reproducibility of nitrogen released as NH_3 for Liquor 3 at 900 °C. The standard deviation for the measurements is 1.06.

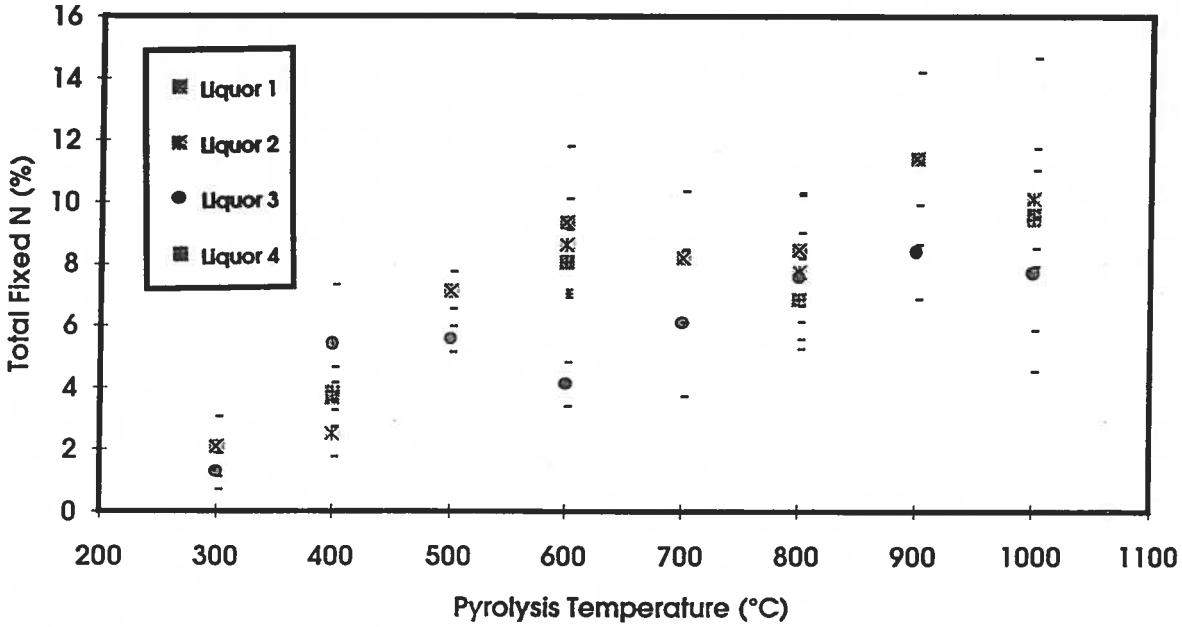

Figure 10. Total N_{fix}, expressed as percent of original liquor nitrogen, for four liquors at pyrolyzed in an N_2 environment at temperatures from 300-1000 °C.

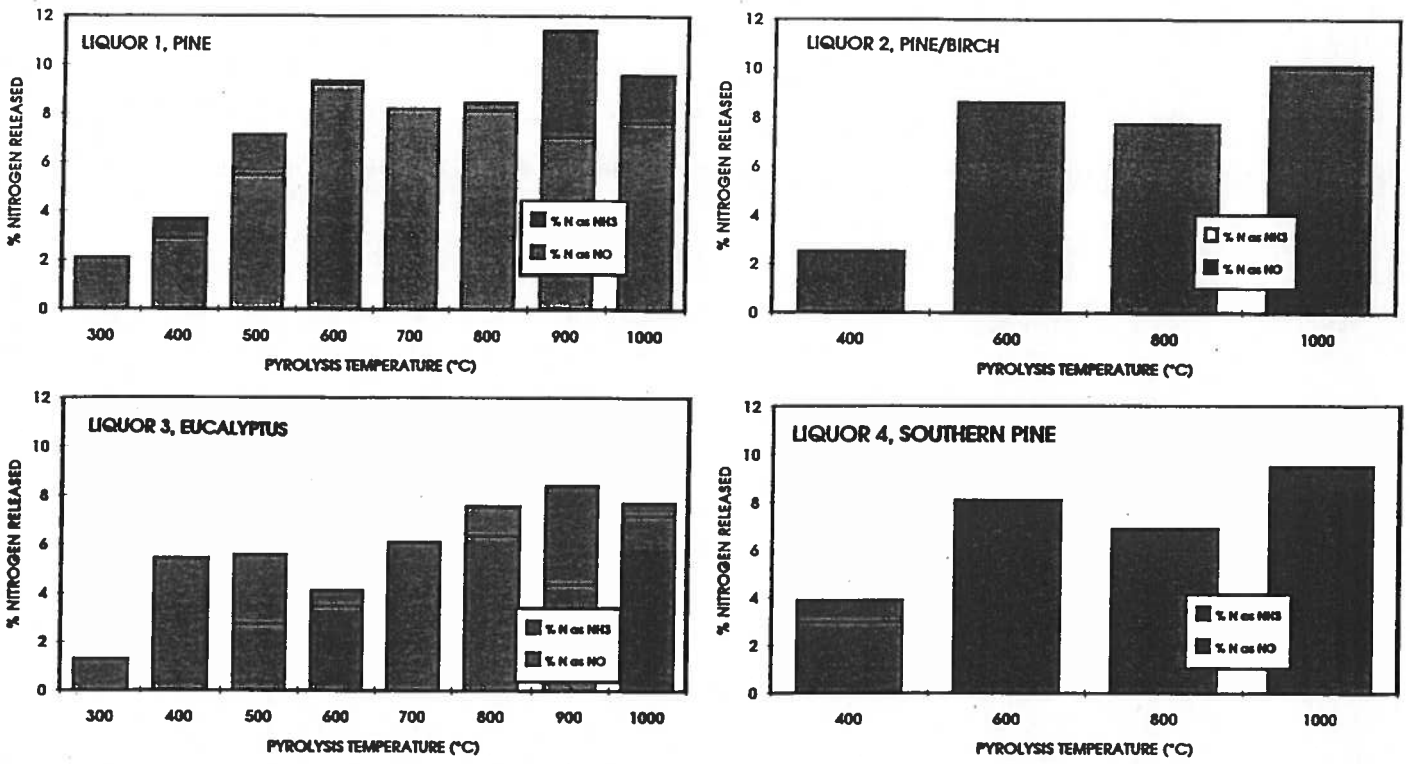

Figure 11. The total N_{fix}, expressed as percent of original liquor nitrogen, as indicated by the sum of the nitrogen released as NO and as NH_3 for four liquors pyrolyzed in N_2 at 300-1000 °C.

The reproducibility of the measurements for NO and NH_3 is indicated in Figures 12 and 13, respectively. The numeric averages and the standard deviations for the experimental nitrogen release are given in Appendix C. All analyses results for the nitrogen remaining in the char had not been received at the time of this writing. However, the results for those that have been received (pyrolysis at 800 °C for Liquor 1) indicated that about half (48 %) of the nitrogen remainded in the char and approximately half was released into the gas phase. This result was similar to Aho's result in that 20-60 % of the original fuel nitrogen was reported to be released during devolatilization. Approximately 2-10 % of the liquor nitrogen, as observed previously in Figure 10, was released as N_{fix} which is lower than but also roughly on the same order as Aho's reported 10-30 % N_{fix}. Then, for the gas phase nitrogen, about 20 % was released as N_{fix}. The remainder of the released fuel nitrogen, therefore, was likely N_2. The nitrogen release pathways for the findings of these experiments, based on the original fuel nitrogen content of the liquors, can be summarized as illustrated in Figure 14.

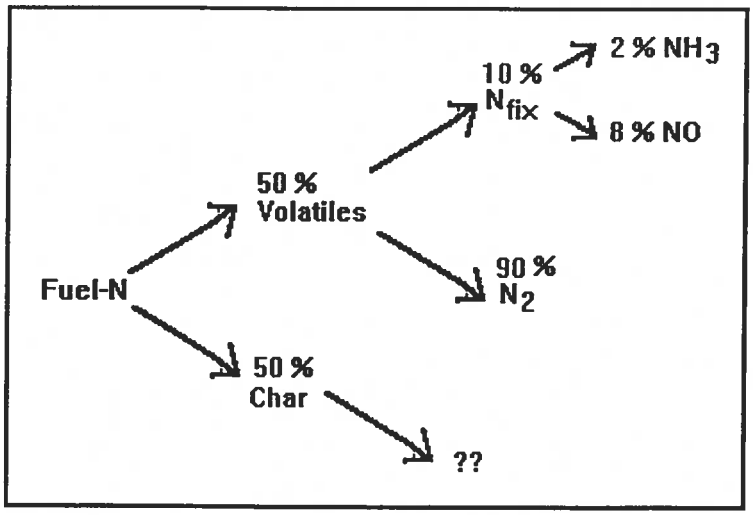

Figure 14. Fuel nitrogen pathway for black liquor pyrolysis, based on original liquor nitrogen content.

Most the nitrogen released was observed to be NO for all liquors and very little NH_3 was found to be present. The greatest amount of NH_3 observed was in the range of 30-50 % of the total N_{fix}, while the average contribution of NH_3 to the total N_{fix} was in the range of 10-12 %. A low level of NH_3 was observed for all liquors pyrolyzed in this study. This opposes Aho's findings where the major portion of the N_{fix} was NH_3. Differences in the experimental set up may provide possible explanations. First, the droplet size in these experiments was significantly smaller than in Aho's study. Droplets from 15-25 mg were used here, whereas the droplets were 35-80 mg in Aho's work. The difference in droplet size would significantly effect the heat and mass transfer rate that the droplets experience.[2] The drying and pyrolysis likely occurred at a faster rate in this study releasing a greater portion of the volatile nitrogen in a shorter time period. The possibility then exists for the nitrogen initially released as NH_3 to find the surrounding environment to be oxygen lean and be converted to N_2 rather than NO. The rate of nitrogen release is known to be strongly dependent on the local temperature and stoichiometry of the combustion environment.[3] Second, the residence time of the gases may be longer in the current set up than in Aho's experiments. This would allow greater opportunity for secondary reactions to occur minimizing the observation of the reactive NH_3 intermediate species. Third, the level of oxygen used in this study was 8 % while in the preivous study about 1.1 % oxygen was used.[4] Finally, the liquors used in the these experiments are not the same as those used in Aho's work. The nitrogen release during black liquor combustion has been noted to be liquor specific.[1]

The greatest release of nitrogen as NH_3 was observed for the eucalyptus black liquor, liquor 3, and for the pine black liquor, liquor 1. Liquor 3 had the highest nitrogen content at 0.09 %. It is known in other combustion processes that an inverse relationship exists between the fuel nitrogen content and the conversion to NO.[5] At low nitrogen content, a greater conversion of the fuel nitrogen to NO was observed. This was also seen in Figure 11 with liquors 2 and 4, where the nitrogen content was 0.07 % and 0.06 %, respectively. Nearly 100 %

of the N_{fix} was NO for both liquors at nearly all temperatures tested. Liquor 1, which had a 0.06 % N content, exhibited a relatively high level of NH_3 in the N_{fix}, as great as 50 %. However, the relative standard deviation of the NH_3 measurements was quite large (see Appendix C) relative to the average values, especially at the higher pyrolysis temperatures. Therefore, some of the higher NH_3 concentrations in these cases may have been due to experimental error.

As noted previously, an increase in the N_{fix} release with an increase in the pyrolytic temperature was observed with all liquors. This was expected based on previous results[1] as well as the fact that greater volatiles release occurs with higher temperatures and heating rates.[2] It should also be noted that the nitrogen release seemed to follow the general trend for droplet swelling at various pyrolysis temperatures (see Figure 11, liqours 1 and 3). At the lowest temperatures, the degree of swelling was small. The swelling increases with increasing temperature to a maximum around 800 °C and at higher temperatures, the char becomes slightly more dense. This was visibly observed for the chars obtained in these experiments. The swelling is dependent on the individual liquor characteristics (viscosity and surface tension) as well as on the pyrolysis conditions.[2] Liquor swelling increases the porosity of the droplet and in turn the heat and mass transfer rates allowing greater volatiles release. However, no good correlations between volatiles yield and swelling currently exist.

CONCLUSIONS

Several conclusions from these experiments should be restated. Concerning the calibration of the analyzers for the measurement of NO and NH_3 in the pyrolytic gases, it was found that the experimental system was satisfactory to measure the volatile nitrogen released as NO and NH_3. In tests measuring known concentrations of NO and NH_3 gases, no systematic error was observed and therefore, no bias in the measurements was indicated. The stability of the analyzers allowed all measurements, even at low concentrations in the range of 1-5 ppm, to be made within 10 % of the true values based on the established calibration curves.

The results of the nitrogen release for black liquor pyrolysis indicated that approximately half of the liquor nitrogen was released in the first stages of combustion. Approximately 2-10 % of the liquor nitrogen was volatilized to N_{fix}, as NO and NH_3, with the remainder of the volatilized nitrogen likely being N_2. The N_{fix} was largely composed of NO with approximately 10-12 % as NH_3 based on the average of all pyrolytic temperatures. The greatest percentage of NH_3 as N_{fix} was in the range of 30-50 %. An increase in the N_{fix} was observed with increasing temperature and likely follows the increase in swelling and porosity which characteristically occurs during black liquor pyrolysis. The increase in the nitrogen release with increasing liquor nitrogen content, has not been verified in the results presented here. Complete char nitrogen analyses should provide a better perspective on this trend.

FUTURE WORK

1. Complete data analysis and documentation of work completed at Åbo Akademi. The documentation of lab work must be completed prior to my return to the Institute so that the project work can continue smoothly in the CCRG.

2. Upon returning to the Institute, a plan to continue work with the TG-DSC will be developed. The results of the factorial screening experiments will serve as the basis for further experimentation.

3. Operation of and calibration techniques for the Antek nitrogen analyzer will be learned. Test methods for the liquor and char samples also have to be developed.

4. Preparations will be made to present the "fifth quarter" seminar. The presentation will tentatively be given in January.

ACKNOWLEDGEMENTS

The author would like to acknowledge the help and assistance of all members of the CCRG in the completion of the work presented in this report, particularly those members who participate in black liquor research. The time spent doing this research was both technically and culturally expanding, both of which are important in the technologically advanced and global pulp and paper industry. Specifically, I wish to thank Mikael (Peppe) Forssén for laboratory and practical assistance in making my transition into the project and otherwise go smoothly. Thanks, also, to Kirsi Laaksonen for helping me find my way in the laboratory and for numerous other times when I needed assistance. Also, my appreciation is extended to Professor Mikko Hupa for providing the opportunity to do joint research within the CCRG and for encouragement and technical advice on many of the challenging problems which occurred during this work. Finally, thanks to everyone who provided answers to my many questions both technical and non-technical. My time spent in your company will be reflected by my broader perspective of nitrogen release during black liquor pyrolysis as well as of life in general.

Likewise, recognition also is given to The Institute of Paper Science and Technology and its member companies for providing funding for this work. Also, the Institute is acknowledged for recognizing the importance of such international cooperations and for allowing me to openly participate in this combined effort.

LITERATURE CITED

1. Aho, K.; Hupa, M.; Nikkanen, S. "Release of Nitrogen Compounds During Black Liquor Pyrolysis." Tappi Engineering Conference Proceedings, Orlando, FL, September 1993.

2. Adams, T. N.; Frederick, W. J. Kraft Recovery Boiler Physical and Chemical Processes. The American Paper Institute, Inc., New York, NY, 1988.

3. Levy, A. "Unresolved Problems in SO_X, NO_X, and Soot Control in Combustion." The Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA. pp. 1223-1242 (1982).

4. Aho, K. "Nitrogen Oxides Formation in Recovery Boiler." Licentiate Thesis, Åbo Akademi University, Turku, Finland. Unpublished. 1993.

5. Chen, S. L.; Heap, M. P.; Pershing, D. W.; Martin, G. B. "Influence of Coal Combustion on the Fate of Volatile and Char Nitrogen During Combustion." The Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA. pp. 1271-1280 (1982).

APPENDICES

The following appendices contain further experimental details or calculations that were made for various portions of the research. Results not presented in the main body of this report or presented in a different fashion are included here, as well.

APPENDIX A: Calculation of Reynolds number for the gas flows during the nitrogen release experiments.

To determine if the system is in the laminar or turbulent regime, the Reynolds number calculation was used. Here, the Reynolds number (Re) is equal to the inertial force over the viscous force.[A1]

$$Re = d\,u\,\rho / \mu = d\,G / \mu,$$

where d is the diameter (in meters) of the flow chamber, ρ is the density of the gas (kg/m^3), μ is the viscosity (kg/m·s), and u is the velocity of the gas (m/s). A Reynolds number less than 2100 represents laminar flow and one greater than 4000 represents turbulent flow. The density of air was taken to be 1.205 (kg/m^3) at 20 °C and 1 atm.[A2] The equation for a cylinder volume was $\pi r^2 h$. The area of a cylinder was $2\pi rh$. The reactor is 3.5 cm in diameter and 52 cm in length. Therefore, the reactor area was 0.5718 m^2. The flow rate at 300 l/h is equivalent to 8.3×10^{-5} m^3/s. Therefore, the velocity was 1.457×10^{-5} m/s. The Reynolds number in the reactor was:

$$Re = \frac{(0.035\ m)\,(1.457 \times 10^{-5}\ m/s)\,(1.205\ kg/m^3)}{(2.05 \times 10^{-5}\ kg/m{\cdot}s)} = 0.02969.$$

Therefore, the gas flow through the reactor was in a laminar regime. At the location of the air addition to the gas sample stream, the flow rate was 53 l/h in a gas line 88 cm in length and 1.25 mm in diameter. The area of the gas line was determined to be 0.0069 m^2. The velocity was 0.00213 m/s and the resulting Reynolds number was:

Yaj Why calculate Re numbers of ~200 in the Sidecase project for gas flow around a pyrolyzer BL droplet

$$Re = \frac{(0.00125\ m)\ (0.00213\ m/s)\ (1.205\ kg/m3)}{(2.05 \times 10\ -5\ kg/m.s)} = 0.1565.$$

Again, the Reynolds number indicated the flow in the gas line to be laminar. The experimental set up should allow for the gases to move through the reactor and gas lines evenly. Therefore, any variation in the analyzer response should not be due to turbulent flows.

A1. Perry, R. H.; Green, D. W., Eds. Perry's Chemical Engineers' Handbook. 6th Ed., McGraw Hill Book Company, New York, NY, 1984.

2A. Levenspiel, O. Engineering Flow and Heat Exchange. Plenum Press, New York, NY, 1984.

APPENDIX B: Determination of statistically sound sample size.

The sample size required to get statistically sound data during the pyrolysis experiments was determined. The data from Aho's experiments was used in the calculation as the same techniques were employed under similar operating conditions.[4] The sample size determination calculation was:[B1]

$$n = [Z_{\alpha/2} \sigma / E]^2$$

where

$$E = Z_{\alpha/2} (\sigma / \sqrt{n}) \quad \text{(where } \sigma \text{ is known or } n > 30)$$

or

$$E = t_{\alpha/2} (s / \sqrt{n}) \quad \text{(where } n \leq 30).$$

Because the sample size is known to be less than 30, the second equation is used to determine E by using the experimental data from Aho's work. During pyrolysis of a birch liquor, the nitrogen released was observed to be 24.1 mg N / 100 g BLS $\pm$ 2.2 mg N/100 g BLS, where nine liquor droplets were pyrolyzed. Therefore, at a 95 % confidence interval, $\sigma = 0.05$ and $\alpha/2 = 0.025$. Thus, $t_{\alpha/2} = 2.306$ where the degrees of freedom are (n-1) = 8. From statistical tables, Z = 1.96. Sustitution of these values to solve for E gives

$$E = (2.306)\ (2.2/\sqrt{9}) = 1.69107.$$

Substitution of E into the first equation, results in ....

$$n = [(1.96)(2.2)/(1.96107)]^2 = 6.5.$$

Therefore, seven replicates was sufficient to provide statistically sound data during the pyrolysis experiments.

B1. Warpole, R. E.; Myers, R. H. Probability and Statistics for Engineers and Scientists. Fourth Edition. MacMillian Publishing Company. New York, NY. 1989.

APPENDIX C: Experimental Standard Deviations for Nitrogen Release Experiments

Standard Deviations reported below were calculated for a sample measurements.

LIQUOR 1, PINE

Fumace temp.	Average % Volatiles Yield	Std. Dev. (Sample)	Average % N as NO	Std. Dev. (Sample)	Average % N as NH3	Std. Dev. (Sample)	Total Fixed N
300	12.23	1.57	2.08	0.39	0	0.57	2.08
400	23.49	0.83	2.9	0.52	0.77	0.44	3.67
500	29.47	0.25	5.47	0.28	1.65	0.33	7.12
600	31.84	2.36	9.2	2.1	0.13	0.34	9.33
700	33.07	1.62	8.2	1.26	0	0.86	8.2
800	36.61	2.2	8.11	1.07	0.34	0.75	8.45
900	73.18	2.08	7.02	0.5	4.38	2.28	11.4
1000	78.48	2.05	7.63	3.96	1.95	1.1	9.58

LIQUOR 2, PINE/BIRCH

Fumace temp.	Average % Volatiles Yield	Std. Dev. (Sample)	Average % N as NO	Std. Dev. (Sample)	Average % N as NH3	Std. Dev. (Sample)	Total Fixed N
400	22.87	1.25	2.5	0.28	0	0.47	2.5
600	31.27	1.42	8.61	1.05	0	0.42	8.61
800	40.18	3.82	7.72	1.38	0	1.11	7.72
1000	77.69	2.83	10	1.35	0.1	0.26	10.1

LIQUOR 3, EUCALYPTUS

Fumace temp.	Average % Volatiles Yield	Std. Dev. (Sample)	Average % N as NO	Std. Dev. (Sample)	Average % N as NH3	Std. Dev. (Sample)	Total Fixed N
300	8.73	1.19	1.28	0.26	0	0.32	1.28
400	23.2	2.85	5.41	1.23	0	0.67	5.41
500	30.32	0.9	2.73	0.22	2.82	0.19	5.55
600	29.74	1.82	3.47	0.38	0.62	0.33	4.09
700	33.36	1.13	6.08	0.68	0	1.69	6.08
800	47.31	0.88	6.36	0.83	1.18	0.61	7.54
900	76.92	1.92	4.36	0.46	4.02	1.06	8.38
1000	78.49	1.28	7.18	1.5	0.49	0.34	7.67

LIQUOR 4, SOUTHERN PINE

Fumace temp.	Average % Volatiles Yield	Std. Dev. (Sample)	Average % N as NO	Std. Dev. (Sample)	Average % N as NH3	Std. Dev. (Sample)	Total Fixed N
400	21.46	0.78	2.97	0.11	0.89	0.17	3.86
600	28.53	2.88	8.05	0.64	0	0.39	8.05
800	42.83	3.42	6.85	0.55	0	0.76	6.85
1000	79.03	2.07	9.43	1.51	0.02	0.06	9.45

RELEASE OF NITROGEN COMPOUNDS DURING BLACK LIQUOR PYROLYSIS

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ABSTRACT

Black liquor droplets were pyrolysed in a tube furnace in argon. Release of nitrogen compounds during pyrolysis was measured for ten different black liquor samples.

Depending on liquor, the fraction of nitrogen release during devolatilization was 20-60% of the original fuel nitrogen.

Ammonia was the primary fixed nitrogen compound released during black liquor pyrolysis. This was verified with two independent analysis methods. Except ammonia small amounts of nitrogen oxide and some molecular nitrogen were also released during the pyrolysis. No hydrogen cyanide was detected.

10-30% of fuel nitrogen was released as fixed nitrogen compounds, N_{fix} (NH_3 and NO). The rate of release of fixed nitrogen was found to increase with increasing temperature.

The yield of N_{fix} released during pyrolysis of different liquor types varied a lot and was proportional to nitrogen content of liquor. Also, conversion of N to N_{fix} increased with increasing nitrogen content of liquor.

INTRODUCTION

The importance of fuel nitrogen in recovery boiler NO_x formation has being discussed in several recent papers. Nichols et al. /1, 2/ have investigated the relative importance of fuel NO_x and thermal NO_x in black liquor combustion. After laboratory measurements they concluded that fuel NO_x represents the major source of total NO_x emitted from recovery furnaces.

The nitrogen content of black liquors is low, typically 0.1% of dry solids. However, approximately 20% of this amount is enough to produce the typical level of NO_x emission of recovery boilers.

In this work we studied the fuel nitrogen behavior during single black liquor droplet burning. The major objectives of the work were to provide information of intermediates of nitrogen compounds formed during combustion of black liquor, and to determine to what extent and at which stage of the combustion process the fuel nitrogen is released. The experiments were concentrated to the devolatilization stage because a major fraction of the fuel-bound nitrogen was assumed to be released during this stage. Pyrolysis is also the stage that can be greatly affected by the combustion technology.

NO_x emissions vary from boiler to boiler. This is affected by the operation of a boiler, as well as the black liquor properties. In this work the nitrogen release was examined during pyrolysis of a number of different types of liquors. One objective was to investigate the differences between liquors originated from different wood species. The results of these laboratory pyrolysis studies were also correlated with emission measurements in some boilers fired with the similar type of liquors.

EXPERIMENTAL

Black Liquor Samples

Three of the black liquor samples studied represented different laboratory pulping conditions and seven samples were mill liquors. Some properties and composition data of the liquor samples studied are shown in table 1 and 2.

Table 1. Properties of the liquors studied (ds = dry solids, HHV = higher heating value, LHT = liquor sample treated in a liquor heat treatment system /3/).

Sample	ds %	HHV MJ/kg ds	N % ds
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 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/50% birch	68.1	14.71	0.141 ± 0.013
7 mixed 50% pine/50% birch LHT	65.3	14.85	0.140 ± 0.014
8 pine, mill	65.6	14.96	0.120 ± 0.009
9 pine, mill LHT	59.1	14.52	0.106 ± 0.014
10 bagasse, mill	71.7	14.90	0.478 ± 0.028

Table 2. Elemental composition of the liquors studied. Percent of dry solids, ds. The balance is mostly fuel bound oxygen.

Sample Nr	Na % ds	K % ds	Cl % ds	S % ds	C % ds	H % ds	Balance % ds
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% ds

Experimental Apparatus and Test Conditions

Black liquor droplets were heated in a laboratory tube furnace in argon. The nitrogen compounds, NO and NH_3(+HCN), released during this heating were measured.

The progress of the liquor devolatilization was followed by measuring the content of carbon monoxide of the gases produced. The experimental set up is shown in figure 1. The pyrolysis reactor was the same as previously used for sulfur release experiments by Frederick et al. /4/.

In each experiment, a single droplet of liquor was suspended on a platinum hook, lowered into the reactor and removed after 300 seconds. The droplets were weighed before and after the pyrolysis. The measurements were repeated 4-15 times (av. 8.5) using different droplet sizes (35-80 mg). The furnace temperature was varied between 300 and 950°C.

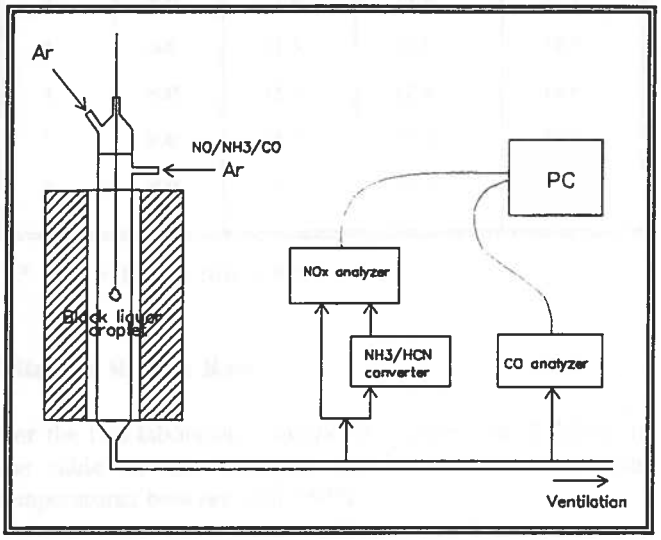

Figure 1. The experimental set up for the determination of nitrogen compounds release during black liquor pyrolysis /4/.

Additional pyrolysis tests were made for larger liquor samples in a muffle furnace. The amount of volatile compounds and the amount of fuel nitrogen released were determined by treating the black liquor in a crucible for one hour at 400°C and measuring the weight and nitrogen content of samples before and after the test.

Analytical methods

NO content of pyrolysis gas was analyzed by a Monitor Labs chemiluminescence based Nitrogen Oxides Analyzer Model 8840.

The sum of **NH_3** and **HCN** in the pyrolysis gas was analyzed by a NO_x analyzer with Monitor Labs Thermocon Converter.

NH_3-content separately was analyzed with an Orion 95-12 ion selective electrode in the H_2SO_4 trapper solution.

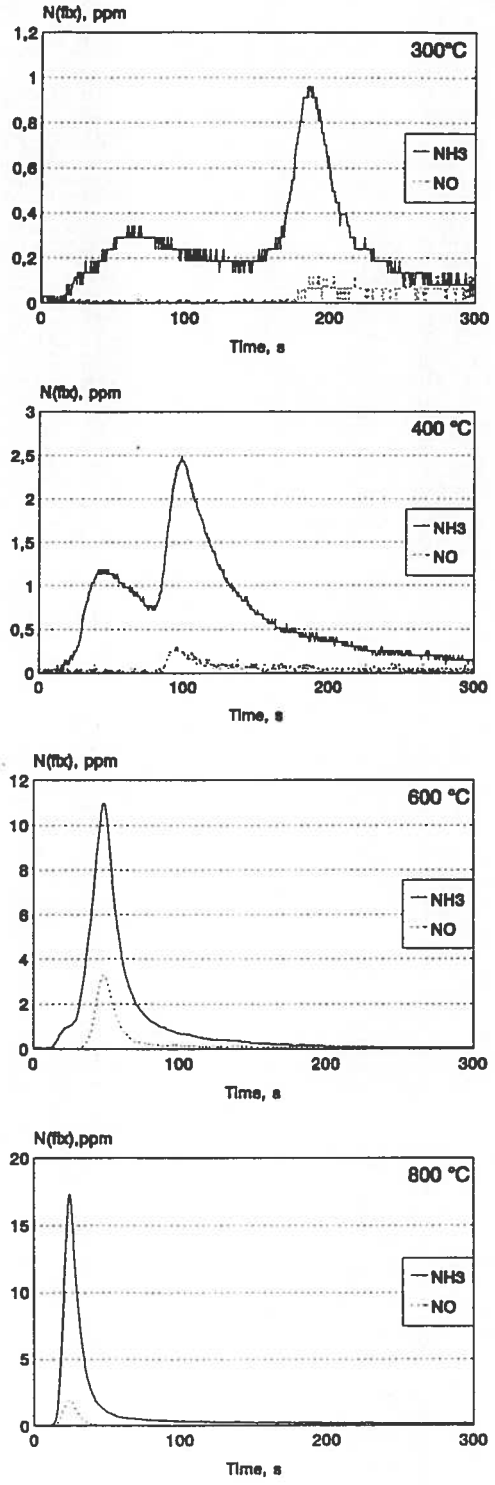

Figure 2. Release of nitrogen compounds during pyrolysis of the liquor Nr.2 at temperatures 300-800°C.

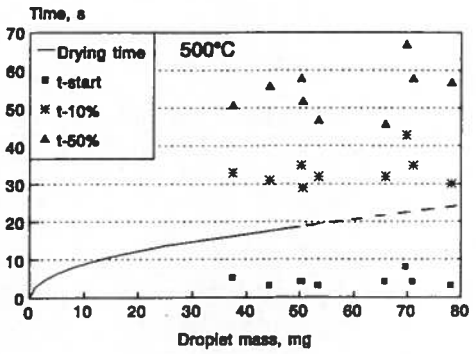

Figure 3. Calculated drying time (solid line) and release of NH_3 during pyrolysis of the liquor Nr.2 at 500°C. The squares indicate the times when first signal was detected (t-start), the asterisks the times when 10% of the total NH_3 was released (t-10%), and the triangles the times when 50% of the total NH_3 was released (t-50%).

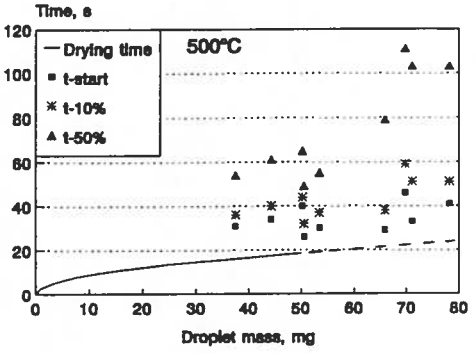

Figure 4. Calculated drying time (solid line) and release of NO during pyrolysis of the liquor Nr.2 at 500°C. The symbols as in figure 3.

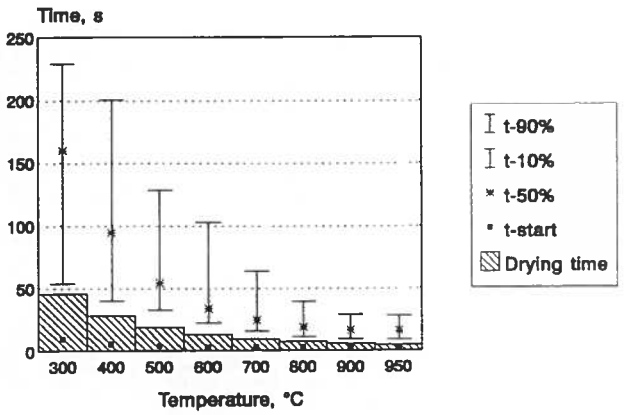

Figure 5. Calculated drying times (shaded) and release of NH_3 during pyrolysis of liquor Nr.2 at temperatures 300-950°C. The vertical lines indicate the time periods during which 80% (from 10 to 90%) of total NH_3 were released.

The squares indicate the times when first signal was detected and asterisks the times when 50% of the total NH_3 was released.

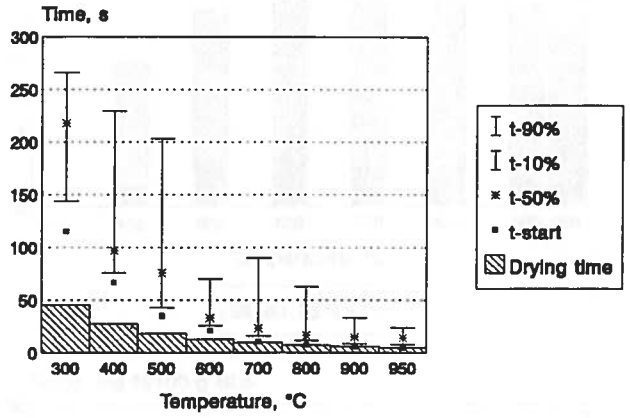

Figure 6. Calculated drying times (shaded) and release of NO during pyrolysis of liquor Nr.2 at temperatures 300-950°C. The symbols as in figure 5.

The times for the release of 50% of the ammonia and nitric oxide, t-50% were determined for both of the liquors 1 and 2. The values for the t-50% were evaluated by integrating from the starting point of pyrolysis to the point where one half of each of the nitrogen compounds respectively were released. Apparent activation energies for each release processes were estimated based on the slope of the Arrhenius type plots like the one shown in figure 7 for ammonia release. The apparent activation energy values for ammonia release were 23 kJ/mol for the liquor Nr.2 and 25 kJ/mol for the liquor Nr 1. Corresponding values for the NO release were 29 and 30 kJ/mol.

These results were obtained in the same way as previously shown for sulfur release from black liquor pyrolysis by Frederick et al. /4/. The estimated activation energy for sulfur release was 26 kJ/mol at the temperature region 350-675°C. This suggests that nitrogen and sulfur release processes during pyrolysis are closely related.

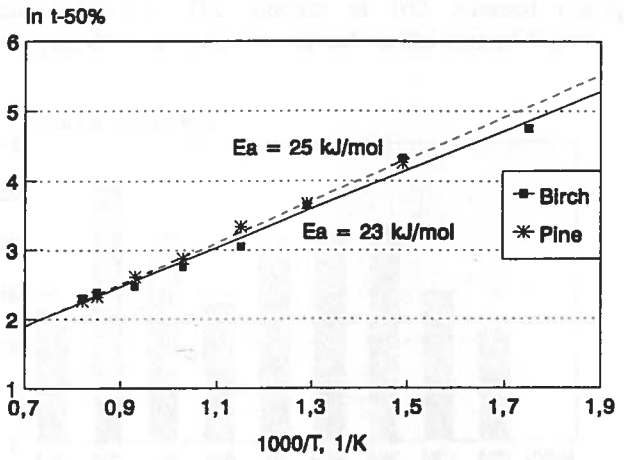

Figure 7. Arrhenius plot for NH_3 release from the pine (Nr.1) and the birch (Nr.2) liquors within the temperature range 300-950°C. Droplet size 40-50 mg.

Total Yield of N_{fix} during Pyrolysis

The total yield of fixed nitrogen (N_{fix} = NO + NH_3) per 100 g BLS are shown in figure 8. These data are based on integration of the release vs. time curves like those in figure 2. Integration time in these measurements was extended to 300 seconds because of the slow rate of pyrolysis at low temperatures. The amount of N_{fix} released at temperatures 300 and 400°C can in reality be somewhat bigger than determined here, but after 300 seconds the nitrogen levels were too low to be detected with the analysis method used.

The results indicate that the level of N_{fix} released from the birch liquor (Nr.2) was nearly twice of the level of the pine liquor (Nr.1). The yield vs. temperature trends have a similar shape for both liquors with a maximum at 700-800°C. At higher temperatures the release of N_{fix} decreases, which may be a result of increased secondary reactions in the pyrolysis gases, where NH_3 and NO may be converted to molecular nitrogen.

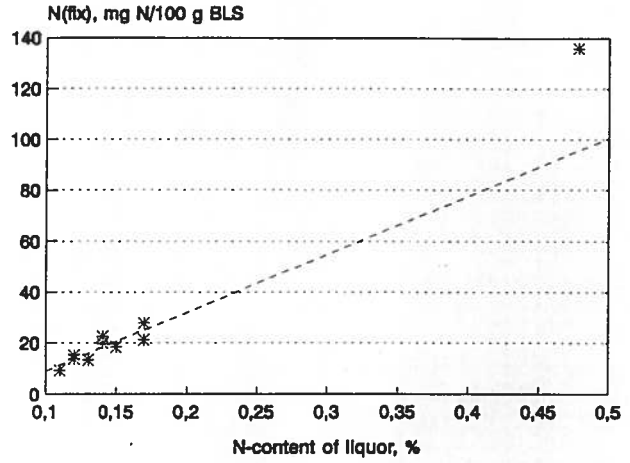

Figure 10. Total release of fixed nitrogen during black liquor pyrolysis at 800 °C as function of nitrogen content of liquor.

Fuel Nitrogen Balance during Devolatilization

To be able to close the nitrogen balance during the devolatilization process some additional tests were made. In these tests the total fuel nitrogen released during pyrolysis was determined by analyzing the nitrogen content in the fuel before the devolatilization test and the nitrogen content in the char after the test. These tests were made for somewhat larger liquor samples in a muffel furnace. By this procedure the amount of total fuel nitrogen released during pyrolysis, vol-N, which besides the fixed nitrogen compounds NH_3, HCN and NO also contains any molecular nitrogen formed, could be determined.

The amounts of total volatiles and vol-N during one hour pyrolysis in muffel furnace at 400°C are shown in table 4. Vol-N were calculated based on nitrogen analysis of original samples and char residues. No systematic variations in the amount of total volatiles or vol-N between different wood species could be found but the bagasse liquor was again an exception.

Based on these tests we can roughly estimate the main reaction routes of the fuel nitrogen during black liquor pyrolysis. This is shown in figure 11. Around 20-60% of the fuel nitrogen is released during the pyrolysis as volatile nitrogen compounds, vol-N. Roughly half of the vol-N is molecular nitrogen, N_2. The other half is mostly ammonia, NH_3.

Table 4. The amounts of total volatiles, and N volatiles during one hour pyrolysis in muffel furnace.

Sample	vol. % ds	vol-N, %
1 Pine	34.0	17.5
2 Birch	36.9	37.6
3 Birch, LHT	36.8	41.4
4 Pine	33.1	21.4
5 Birch	32.8	20.3
6 mixed	28.2	18.5
7 mixed, LHT	27.0	27.0
8 Pine	29.2	31.6
9 Pine, LHT	24.3	40.7
10 Bagasse	46.1	64.6

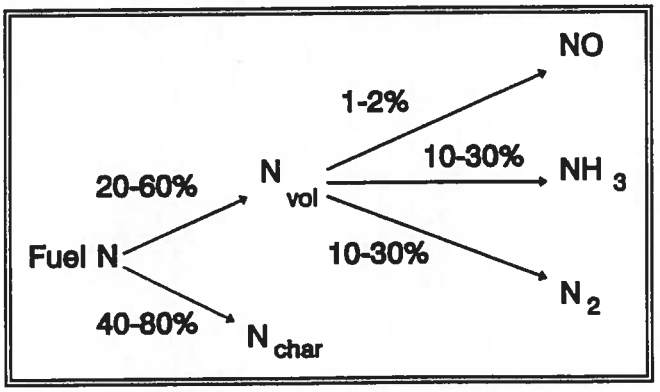

Figure 11. A schematic presentation of the behavior of the fuel nitrogen during black liquor pyrolysis.

Emission Measurements in Recovery Boilers

Figure 12 shows recovery boiler NO_x-emissions in different mills measured recently by Ahlstrom /6/. There are some variations in each boiler, but systematic difference can be seen between different wood species. NO_x-emissions are significantly higher for the birch liquor than for the others. The lowest NO_x emissions were measured for eucalyptus and red wood liquors. The nitrogen contents in the black liquor solids are as follows /6/:

	N in BLS, %
Red wood liquor	0.08-0.10
Eucalyptus liquor	0.10
Pine liquor	0.10-0.19
Birch liquor	0.16-0.19

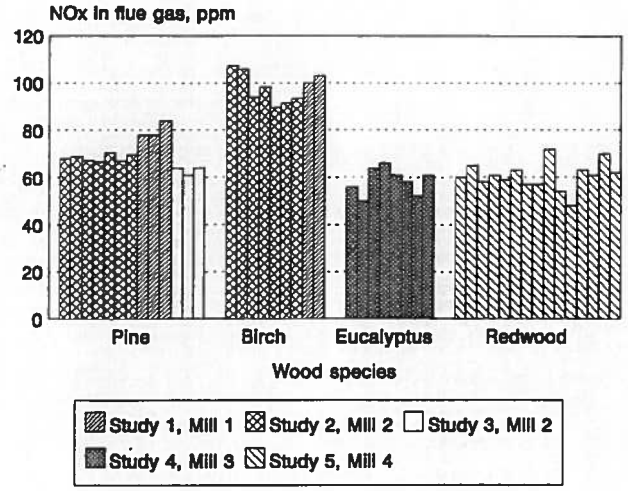

Figure 12. NO_x-emissions in dry flue gases at 8% O_2 in different mills with different wood species.

The results suggest that NO_x-level in recovery boiler flue gases is to a large extent determined by the liquor nitrogen content and thus by wood species used in pulping. Of course the NO_x level is also influenced by the furnace operating parameters, which control the temperature distribution and the local air ratios in the various parts of the furnace.

The results of these mill studies also support the assumption that N_{fix} released during pyrolysis has an important role in formation of nitrogen oxides emissions in a recovery boiler.

CONCLUSIONS

A significant part of the fuel nitrogen was found to be released during the pyrolysis process. Only minor part of the nitrogen may be released during the drying stage. Depending on liquors the fraction of fuel nitrogen released during devolatilization was 20 - 60%.

The main intermediate of fuel nitrogen formed during devolatilization of black liquor was found to be NH_3. Except ammonia and molecular nitrogen, small amounts of nitrogen oxide were released. The common nitrogen intermediate in fossil fuel pyrolysis, HCN, was not detected.

10-30% of fuel nitrogen was released as fixed nitrogen compounds, NH_3 and NO. The rate of release of fixed nitrogen increased with increasing temperature.

The amount of fixed nitrogen, N_{fix}, released during pyrolysis was proportional to the liquor nitrogen content. N_{fix} increased with increasing fuel nitrogen content. The level of N_{fix} released from birch liquors was nearly twice of the level of pine liquors. The yield of N_{fix} from the bagasse liquor was significantly higher than from the others.

The maximum level of N_{fix} release was obtained at the furnace temperature range 600-800 °C.

NO_x emissions of a recovery boiler seem to depend mainly on the nitrogen content of black liquor and thus on the wood species used in pulping. Assuming that all NH_3 released during pyrolysis were converted to NO in the recovery furnace, NO_x-emissions formed by burning the liquors studied would be 31-95 (bagasse 457) ppm (8% O_2), which is exactly in the same range as the typical published NO_x emissions.

REFERENCES

1. Nichols, K.M., Thompson, L.M., Veverka, P.J., Empie, H.J., Lien, S.J., Relative Importance of Fuel-NO_x in Black Liquor Combustion, IPST-Raport of Projects 3670 and 3605-1, Atlanta, 1992, 54 p.

2. Nichols, K.M., Lien, S.J., Formation of Fuel NO_x during Black Liquor Combustion, Tappi Journal, 76(3):185(1993).

3. Nikkanen, S., High Dry Solids Firing, JALO-seminaari 3-4.12.1992, Helsinki.

4. Frederick, W.J., Forssen, M., Hupa, M., Hyöty, P., Sulfur and Sodium Volatilization During Black Liquor Pyrolysis, Tappi, Proceedings of International Chemical Recovery Conference, 1992, pp. 599-608.

5. Frederick, W.J., Combustion Processes in Black Liquor Recovery: Analysis and Interpretation of Combustion Rate Data and an Engineering Design Model, US DOE Report DOE/CE/40637-T8(DE90012712), March, 1990.

6. Ahlstrom, Internal research reports, 1990-1992.

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