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The Impact of Black Liquor Composition on the
Release of Nitrogen in the Kraft Recovery Furnace

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THE IMPACT OF BLACK LIQUOR COMPOSITION ON THE RELEASE OF NITROGEN IN THE KRAFT RECOVERY FURNACE

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ABSTRACT

Results have shown that the composition of the nitrogen species in black liquor is important in the ultimate conversion of fuel nitrogen to NO_x. Two Kraft southern pine liquors with nitrogen concentrations of about 0.06% were used in the study. The nitrogen content of the liquors was shown to be mainly organic, largely as proteinacious compounds, and to be associated with the lignin fraction of the liquor. The various types of nitrogen compounds suggest the possibility of several fuel nitrogen pathways to form NO_x during recovery boiler operations.

Tests using model compounds of these black liquor nitrogen species indicated that the conversion of the bound nitrogen to NO_x varied greatly and was highly dependent on the chemical structure. Along with the dependence of the nitrogen structure on the fuel nitrogen conversion to NO_x, the composition of the matrices, i.e. the inorganics, in which the nitrogen resides also has been shown to be significant during pyrolysis. The results of these investigations have been applied to Kraft recovery operations to suggest possible NO_x control strategies.

Keywords: Black Liquor, Pyrolysis, Combustion, Emission, Fuel Nitrogen, Nitrogen Oxides, NO_x, Recovery Furnace.

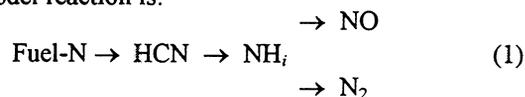
INTRODUCTION

With continued tightening of allowable air emission levels, it becomes increasingly important to understand the source of the emission in order to minimize generation. The emissions of nitrogen oxides (NO, NO₂, and N₂O) are regulated by the 1990 Clean Air Act Amendments. Current allowable emissions are based on site-specific, best-available control technologies and on the region within which the mill resides. Most regulated levels are approaching 100 ppm NO_x, but for some mills located in heavily restricted areas, the allowable limits have dropped to as low as 50 ppm NO_x.¹

The major contributor to the formation of nitrogen oxide emissions from Kraft recovery furnace operations is the

oxidation of the nitrogen in the fuel.^{2,3} This fuel NO_x pathway dominates the thermal NO_x and prompt NO_x pathways due to a relatively low temperature and the absence of hydrocarbons during the combustion of black liquor, respectively. Since greater than 95% of NO_x is NO, NO₂ and N₂O will not be considered. In this paper, the terms NO_x and NO will be used synonymously.

The formation of nitrogen oxide emissions during the combustion of Kraft black liquor is known to result from the fuel NO mechanism. While this mechanism involves literally hundreds of reactions,⁴ the simplified and often used model reaction is:



The NO product of this reaction is dependent on the amount of oxygen available to react with an intermediate species such as HCN and NH_i. In an oxygen-rich environment, NO is expected to be the product; whereas, in an oxygen lean environment, N₂ would prevail. The sum of the intermediates plus NO is defined as fixed nitrogen. Aho, et al.⁵ reported 10-30% of the fuel nitrogen of black liquors to be released both as fixed nitrogen and as N₂ during pyrolysis with approximately 40-80% of the fuel nitrogen remaining in the char. The total nitrogen released as fixed nitrogen increased with increasing temperature with the primary volatilized species being NH₃. It was noted that the fixed nitrogen released during pyrolysis was liquor dependent and proportional to the black liquor fuel nitrogen content.

Current recovery furnace NO_x emissions range from 0-155 ppm (at 8% O₂).³ Considering the average black liquor fuel nitrogen content of 0.1% based on dry solids, current emission levels can be accounted for with only a 20% conversion of the black liquor nitrogen to NO.³ Therefore, the potential exists for the remaining 80% of the nitrogen to be converted to NO. In-situ reactions can occur to account for partial depletion of the NO as it is formed.⁶ However, the question remains as to what parameters control the release of black liquor nitrogen and its ultimate conversion to NO during recovery furnace operations. In this paper, the effects of the black liquor composition, both in terms of the structure of the black liquor nitrogen and the inorganic fraction, are reported for combustion and pyrolysis conditions.

MATERIALS AND METHODS

Black Liquor Characterization

Several commercial Kraft black liquors were used as a basis for this investigation and have been reported previously.⁷ The elemental composition is provided in Table 1. Note

that the elemental composition of these liquors varies both in terms of wood species pulped and also within the same species for different pulping conditions (So. Pines I and II). The nitrogen content of these liquors was less than the 0.1% average reported.

Table 1. Elemental composition of commercial Kraft black liquors reported as weight percent of dry solids.

Commercial Kraft Black Liquor	C	H	N	S	O	Na	K	Cl
Pine	35.8	3.6	0.06	4.6	32.6	21.0	1.8	0.5
Pine/Birch	33.1	3.4	0.07	5.0	30.1	25.9	1.8	0.6
Eucalyptus	37.3	3.6	0.09	3.4	33.2	19.0	1.8	1.6
So. Pine I	34.3	3.4	0.06	5.2	33.4	19.7	3.0	0.9
So. Pine II	31.0	4.1	0.06	2.4	33.8	21.2	1.5	0.6

Fuel Nitrogen Characterization

The nitrogen in black liquor largely comes from the wood and enters the black liquor stream with the lignin in the wash lines after pulping and bleaching.⁸ The nitrogen is present as lignin protein amino acids and other nonproteinaceous compounds. It is also possible for a very small fraction of the nitrogen to enter the black liquor stream through process additives such as defoamers and anti-scaling agents. In most instances, however, these extraneous nitrogen sources can be neglected with respect to the much greater source from wood-lignin. Likewise, nitrogen from additives has not been considered in this work.

To further evaluate the source of nitrogen, a black liquor sample was acidified to precipitate the lignin and determine its nitrogen content. In this procedure, all inorganics and low-molecular-weight carbohydrates were removed to obtain a lignin that is heterogeneous with regard to its chemical properties.⁹ The lignin content of the liquor was approximately 50% of the whole liquor. It was found that its nitrogen content on a dry solids basis was twice that of the whole liquor, indicating that the nitrogen content of the liquor is mainly associated with the lignin fraction.

An evaluation of the types of organic nitrogen in black liquor was made and the results are indicated in Figure 1. As indicated in the figure, the specific types of nitrogen are difficult to quantify due to limits of detection with the analytical methods used. Individual compounds with <2% nitrogen made up 79% of the total organic nitrogen. Nitrogen was found to be present both in straight chains and bound in heterocyclic ring forms.⁷ Qualitatively, the latter were comprised of indoles, pyrazoles, and pyrimidines, representing both five- and six-membered ring structures. Similar heterocyclic structures have been found in birch Kraft black liquor.¹⁰ Because various forms of nitrogen exist, multiple pathways for NO_x formation must be considered.

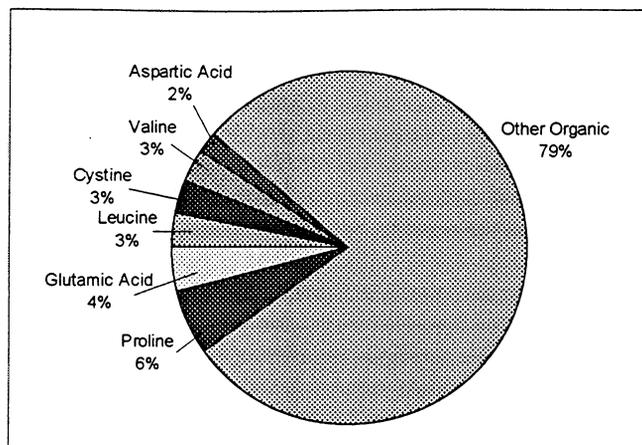


Figure 1. Composition of organic fuel nitrogen species in a southern pine black liquor.

Because of the complexity of the black liquor make up, model compounds of the black liquor nitrogen species were selected to be used for further study. The species included, but were not limited to, glutamic acid, proline, ammonium nitrate, and pyrazine. The structures of these species are provided in Figure 2 below. The nitrogen species were chosen based on the data presented in Figure 1 and species which are used as common analytical nitrogen standards. The nitrogen species were prepared in distilled deionized water at concentrations of 0.001-0.1% N. This is the range of interest for the typical black liquor nitrogen content and its individual components.

Evaluation of these model fuel nitrogen compounds was pursued to understand the individual effects of the nitrogen chemical structure and the inorganic matrices on the conversion of these species to fuel-NO_x, or its intermediates (HCN and NH₃), which occurs during pyrolysis. This method of analysis provides an evaluation of a mill's potential to emit NO_x based on the composition of the black liquor to be fired in the recovery furnace.

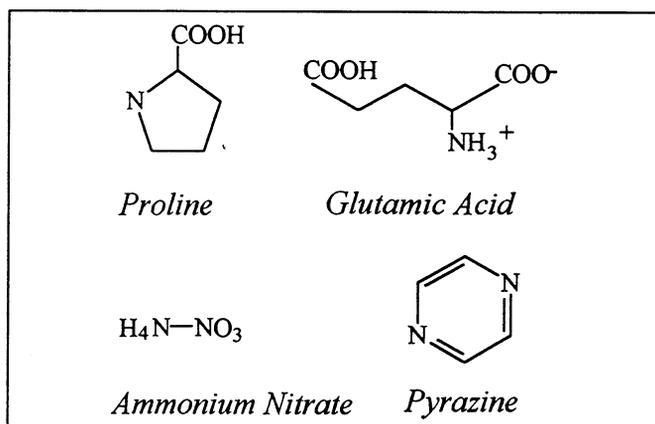
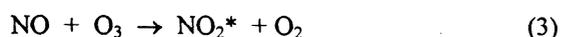
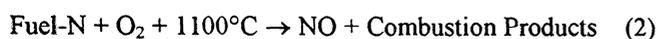


Figure 2. Chemical structure of nitrogen species: glutamic acid, proline, ammonium nitrate (NH₄NO₃), and pyrazine.

Nitrogen Analyzer

High-temperature combustion followed by chemiluminescence detection is a relatively new method used to determine total nitrogen. For many sample types, very good results can be achieved in the range of 0.001-1% N or greater. The method employs combusting a small amount of sample in a high-temperature, oxygen-rich (<75% O₂) environment oxidizing all fixed nitrogen species present. Note that these conditions will not generate thermal NO_x from N₂ in the atmosphere. The oxidized form of nitrogen, NO, then reacts with ozone, O₃, to form excited nitrogen dioxide. As the excited molecule decays, light is emitted and detected with a photomultiplier tube.¹¹ The following equations chemically describe the process.



The total nitrogen result is determined by the light response emitted by the unknown sample compared with that of a known standard material. In this regard, the analysis response is determined like many analytical tests. The calibration standard is used to generate a linear response throughout the concentration range of interest to which the unknown response can be compared.

It has been established that the calibration standard and its matrix must closely represent the type of nitrogen to be analyzed and the matrix of the sample.¹¹ Without closely representing the type of nitrogen structure and the sample matrix, error in the analysis results due to changes in the nitrogen chemistry involved.

The nitrogen analyzer system is shown in Figure 3. A multi-matrix sample drive was used to introduce liquid and solids samples into the analyzer for combustion while the gas sampling inlet system was elicited for controlled introduction of gaseous samples.

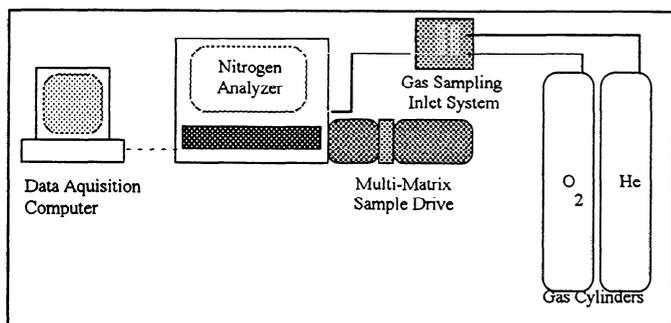


Figure 3. Schematic diagram of nitrogen analyzer system.

Combustion Methods

All combustion conversion experiments were conducted in an 1100°C, 75% O₂ combustion environment to maximize the conversion to NO_x. Pyrolysis experiments were conducted in both oxidative and inert environments under controlled heating rates.

Under combustion conditions, nitrogen measurements were made to test for the effects of several parameters. The relative conversions of the fuel nitrogen to fixed nitrogen (the sum of NO plus any oxidizable intermediates, such as HCN and NH_i) for several nitrogen species were determined. The effect of various sodium salts at equivalent concentrations on the nitrogen response of glutamic acid and the effect of increased sodium carbonate concentration on the nitrogen response of ammonium chloride also were evaluated.

Pyrolysis Methods

Conversion of the fuel nitrogen to fixed nitrogen also was measured under various pyrolytic conditions. Pyrolysis of several nitrogen species were conducted in inert (pure He gas) and oxidative (~15% O₂ in He) environments. The pyrolysis experiments were carried out at heating rates of 50-150°C/min at temperatures from ambient to 700°C. The effect of gas flow rate was evaluated by pyrolyzing the samples both in stagnant and full gas flow (0.170 L/min) environments. The fuel nitrogen conversion to fixed nitrogen was measured using the nitrogen analyzer described previously.

All pyrolysis experiments were carried out in a temperature-programmable furnace, which is attached directly to the nitrogen analyzer. A schematic diagram of the pyrolysis set up is provided in Figure 4. The programmable furnace replaces the multi-matrix inlet. Detailed results for combustion and pyrolysis experiments are presented and discussed in the following section.

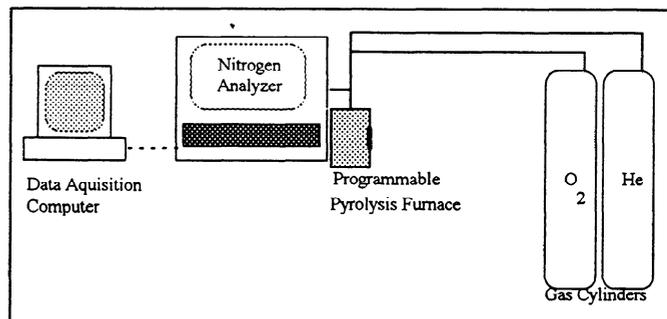


Figure 4. Schematic diagram of nitrogen analyzer system with attachable, temperature-programmable pyrolysis furnace.

RESULTS AND DISCUSSION

Combustion Studies

Comparison of nitrogen conversions. To compare the relative conversions of the nitrogen species, $\text{NO}_{(g)}$ was measured using the nitrogen analyzer within the concentration range of interest. Combustion conditions were used to maximize conversion of the fuel nitrogen to fixed nitrogen measuring $\text{NH}_{3(g)}$ and other intermediate fuel nitrogen species along with NO . Evaluation of the data was made by comparing the slope of the calibration response for each individual species with that of the calibration response of NO . The relative conversions compared to the NO response at equivalent concentrations is provided in Figure 5. The average relative standard deviation (RSD, %) for all analyses was $\sim 5\%$ and the data were quite reproducible. Note that all of the nitrogen species yield less than 100% conversion by comparison to NO . Even the NH_3 yield is low by approximately 17%, suggesting that the NH_3 reacts either with itself (Equation 5) or with NO to yield N_2 , which is not measured in this analysis system.

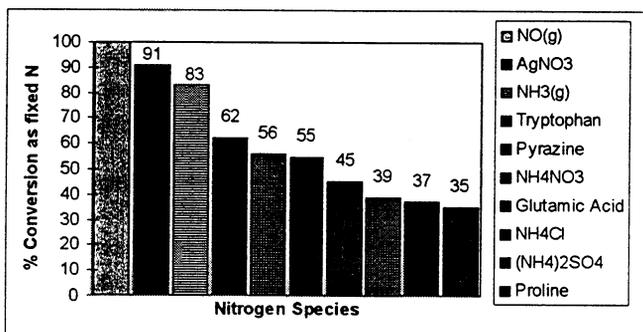
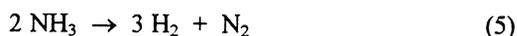


Figure 5. Relative conversions of various nitrogen species with respect to $\text{NO}_{(g)}$.

Explanation of the differences in conversions was sought both in the thermodynamics and kinetics of the combustion environment. It was found that the results of the thermodynamic equilibrium concentration calculations did not follow what was observed experimentally, which suggests kinetic control for the reactions. The thermodynamic calculations indicated no increase in the NO or N_2 concentrations within a temperature range from 100-1100°C. It has been reported that the gas phase nitrogen chemistry does not follow the thermodynamic predictions.¹² If complete mixing occurs, kinetic calculations, evaluating the conversion to NO from both the NH_3 and the HCN intermediate species, predicted complete conversion to NO for analyzer combustion conditions and

for the sizes of the samples used. Complete conversion was not observed, however, which suggests intermediate reactions that generate unreactive N_2 play an important role.

While the differences in conversions are not fully understood, some explanation can be found in the nitrogen chemistry. For example, some species of nitrogen are capable of tautomerization, allowing stronger bonds to form within the structure. This would be particularly true of heterocyclic compounds. Structures such as proline tend to have a refractory nature to high-temperature oxidation and yield molecular nitrogen (N_2) instead of nitric oxide.¹³ Other structures, where an N-N bond exists in a five- or six-membered ring coupled to an N=C, are able to tautomerize, shifting the double bond around the ring forming the stronger N=N bond. However, the conversions of these species to NO can be improved if highly electronegative substituents, such as sulfur, are located on the ring withdrawing the electrons to prevent the N=N bond from forming.

The conversions of the ammonium species are similar especially for the NH_4Cl and the $(\text{NH}_4)_2\text{SO}_4$ at about 38% compared to NO . However, the NH_4NO_3 conversion is 55%. The increased conversion is likely due to a portion of the nitrogen in the nitrate form which is noted to have a higher conversion for AgNO_3 . (See Figure 5.) Approximate averages indicate the conversion of either the nitrate or the ammonium forms of nitrogen to remain the same regardless of the compound within which it resides. The other forms of nitrogen as the amine groups vary with respect to their individual bonds and structures.

Effect of matrices on nitrogen conversion. The effect of matrices composition on the nitrogen conversion of fuel nitrogen model compounds was evaluated. Equivalent concentrations of several sodium salts were used as the aqueous matrix for glutamic acid nitrogen. The results presented as the relative conversion to NO are provided in Figure 6.

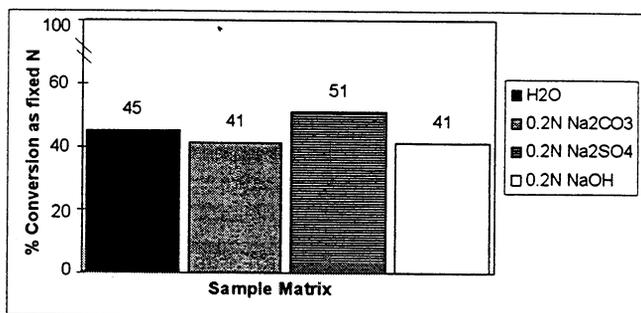


Figure 6. The effect of the matrices on the nitrogen conversion to fixed nitrogen of glutamic acid.

The effect of matrix concentration also was evaluated. Concentrations of sodium carbonate in the range of 0-0.5N Na_2CO_3 made up the matrices for NH_4Cl samples in which the nitrogen conversion to NO was measured. An enhancement of the nitrogen response was observed as the concentration of sodium carbonate in the sample matrix increased. (See Figure 7.)

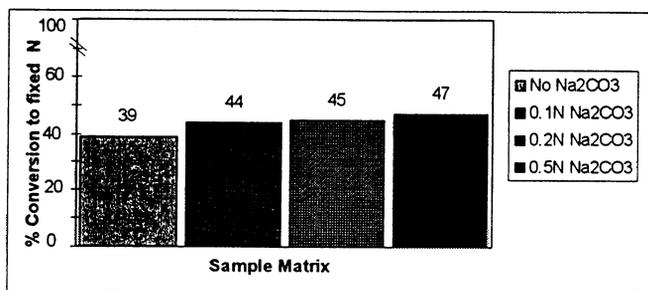


Figure 7. The effect of increased sodium carbonate concentration in the matrices on the nitrogen response of NH_4Cl .

The data show increases in the nitrogen response by 15, 17, and 23%, respectively, for the 0.1N, 0.2N, and 0.5N Na_2CO_3 matrix concentrations. This result opposes the effect observed for the glutamic acid nitrogen response reported in Figure 6. The glutamic acid nitrogen response was lower with a matrix of 0.2N Na_2CO_3 and 0.2N NaOH (by 9% and 10%, respectively), while the response was enhanced by nearly 14% with a matrix of 0.2N Na_2SO_4 . These conflicting results indicate that the matrix effect on the nitrogen response is nitrogen-species specific as well as matrix-species specific. A better understanding of these differences may be sought in understanding the differences in the initial conversions to NO based on the nitrogen chemistry involved and on the pyrolysis studies.

Pyrolysis Studies

Effect of nitrogen source and amount. A series of pyrolysis experiments were conducted, both in oxidative and inert environments, to establish the effects of pyrolysis on the conversion of the model fuel nitrogen species to NO. The pyrolysis experiments were carried out in the attachable, temperature-programmable furnace and the total fixed nitrogen was measured with the nitrogen analyzer as shown in Figure 4. All samples were heated at a rate of $150^\circ\text{C}/\text{min}$ and all of the nitrogen was released for all samples by 400°C . The nitrogen from pyrazine was released at about 40°C , while that of glutamic acid and proline was released at about 90°C and 120°C , respectively.

As indicated in Figure 8, no significant differences ($\leq 3.0\%$ difference for nearly all samples tested) in the pyrolytic release of fixed nitrogen were noted for oxidative vs. inert

conditions. For pyrazine, the difference of about 11% can not be designated to be significant because the reproducibility of the measurement was poorer (Relative Standard Deviation $\cong 13\%$).

The fixed nitrogen released during pyrolysis, either oxidative or non-oxidative, was greater for the glutamic acid and proline nitrogen species than it was for the same species at equivalent concentrations during combustion. It is suspected that incomplete conversion of all of the fixed nitrogen species to NO occurred, and a portion of the nitrogen was released as N_2 . It appears that the pyrolysis conditions have a major effect on the way that the fuel nitrogen is converted—the intermediates either react to form N_2 or are ultimately oxidized to NO.

Pyrazine nitrogen indicated poorer conversion to fixed nitrogen under pyrolytic conditions. This may result in part from the lower heating rates at pyrolysis as compared to those obtained at higher combustion temperatures. The effect of heating rate is a subject of further investigation.

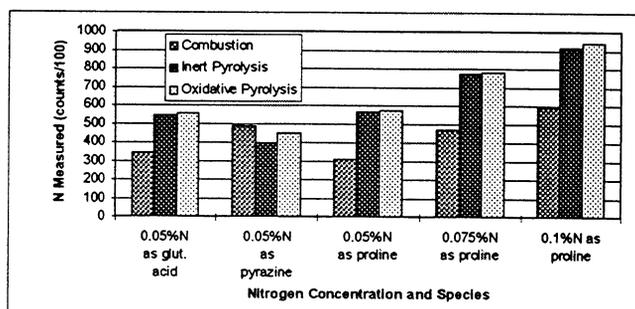


Figure 8. Fixed nitrogen measurements under pyrolysis and combustion conditions (for comparison).

The lower conversion of fuel nitrogen to fixed nitrogen for pyrazine ($\text{C}_4\text{H}_4\text{N}_2$) suggests that the release of oxidizable intermediates and their conversion to NO rather than N_2 occurs within the boundary layer. In the case of pyrazine, no bound oxygen is present as the liquid drop volatilizes. The released nitrogen is then believed to selectively form N_2 in the inert environment as the intermediate species react with each other in the absence of oxygen. This is also supported by the data shown in Figure 12.

Effect of matrices on nitrogen conversion. The effects of inorganic salts in the aqueous matrices on the nitrogen conversion also was tested. The results indicating the comparison between equivalent concentrations of NaOH , Na_2SO_4 , and Na_2CO_3 are given in Figure 9. While the application of the Na_2SO_4 had no significant effect, the use of NaOH and Na_2CO_3 in the matrices decreased the amount of nitrogen measured as fixed nitrogen by 40% and 32%, respectively during slow pyrolysis. It also was noted that

combinations of the sodium salt species in the matrices seem to have an averaging effect. This indicates the anionic form of the sodium salt to be important.

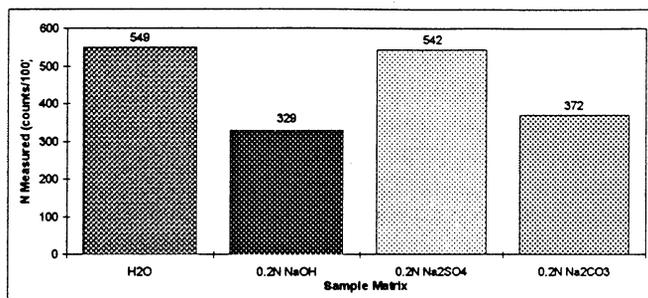


Figure 9. Effect of inorganic species on fuel nitrogen (as glutamic acid) conversion to fixed nitrogen for oxidative pyrolysis conditions (heating rate equaled 150°C/min).

Comparing the effects of the inorganic matrices for oxidative pyrolysis with those from combustion indicated in Figure 6, the data show the same effects. However, the effect of the inorganics does not seem as great in the high-temperature, high-oxygen combustion environment.

The inorganic concentration also is important in understanding the nitrogen release and its conversion to fixed nitrogen. In Figure 10, it can be seen that as the NaOH concentration is increased, the nitrogen measured as fixed nitrogen decreases. Nitrogen profiles of these species indicate that the addition of the sodium salt tends to slightly retard the initiation of the nitrogen release. The corresponding shift in initial nitrogen release temperature is about 20–30°C.

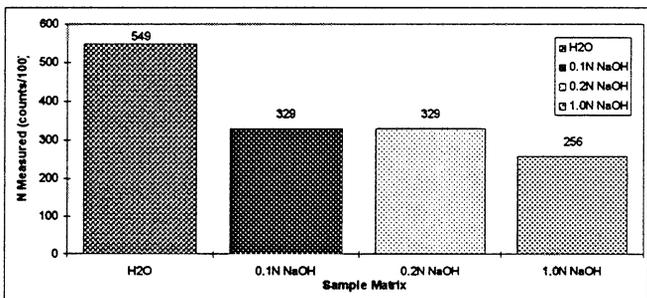


Figure 10. Effect of increasing NaOH concentration on fuel nitrogen (as glutamic acid) conversion to fixed nitrogen under oxidative pyrolysis conditions (heating rate equaled 150°C/min).

Comparison of this result with that of the combustion inorganic concentration is difficult because both the nitrogen species and the inorganic species are different. However, it does again indicate the importance of the fuel nitrogen structure on the conversion to fixed nitrogen.

Effect of residence time prior to combustion. The effect of the pyrolytic gases residence time prior to combustion on the conversion of the fuel nitrogen species to fixed nitrogen was evaluated. Experimentally, stagnant conditions were maintained during the 150°C/min heating up to 400°C. A typical nitrogen profile of the release with time and temperature is provided in Figure 11. Note that the release of pyrolytic gases forces some flow into the combustion area of the detector. The first column (stagnant) for each sample represents the total nitrogen released as fixed nitrogen determined as the area under the first peak in Figure 11. The second column (He added, full flow) represented the total fixed nitrogen released. This is the sum of the first and second peaks. Finally, the last column represents the nitrogen released as fixed nitrogen under pyrolytic conditions with continuous gas flow during heating to and at 400°C.

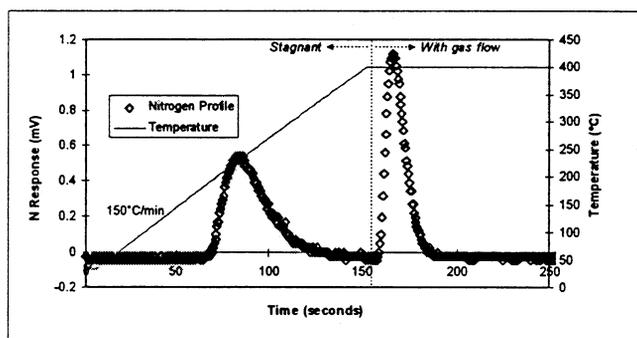


Figure 11. Nitrogen release profile of 0.05%N as proline under stagnant inert pyrolysis conditions.

With the stagnant environment, the conversion to fixed nitrogen is only about 45% for glutamic acid nitrogen and 55% for proline nitrogen compared to that for the same inert conditions with full-time flow.

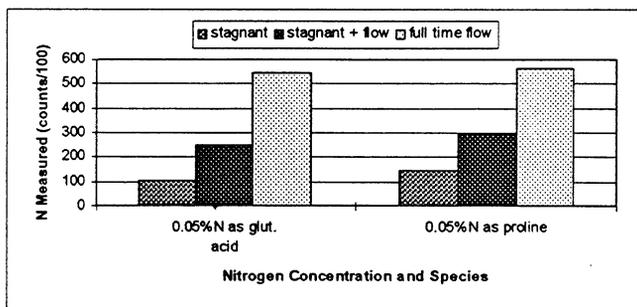


Figure 12. Effect of gas flow on fuel nitrogen conversion to fixed nitrogen during inert pyrolysis.

When stagnant conditions existed, conversion to fixed nitrogen was lower than when the pyrolysis took place with gas flowing over the drop sweeping the pyrolytic gases away. Apparently, the stagnant conditions allowed the fixed nitrogen intermediates, such as HCN and NH₃, to

remain at high concentrations thus being able to react with each other forming N_2 in the oxygen-deprived environment. In the diluted environment, the intermediates were much more dispersed and likely remained as intermediates until undergoing high-temperature, excess-oxygen combustion where the species were easily oxidized in the next chamber of the furnace.

Alternative NO_x Control Strategies

Current NO_x control strategies include the use of biased firing, air staging and low excess air firing, and fuel nitrogen doping.¹⁴ However, these methods were developed for the reduction and elimination of thermal NO_x . These methods may have limited success in a recovery boiler where NO_x emissions are generated from the nitrogen in black liquor. Based on the reported conversions of the fuel nitrogen species and the results of their pyrolysis and combustion, some alternative NO_x control strategies may be available for recovery furnace operations.

The nitrogen species are important with respect to the degree of fuel nitrogen conversion attainable within a combustion environment. The amine type species tend to exhibit lower conversions and therefore, would be the preferable form of nitrogen in the pulp wood. This result is supported by the fact that ammonia and urea nitrogen species (both with R-NH₃ structures) are functional in reducing NO_x when injected into the gas stream.^{15,16} Nitrate species should be avoided as their conversion during combustion remains high regardless of its structural bonding.

Evaluation of the sodium species in the matrices indicates that the inorganic composition of black liquor is likewise important. Modification of the sodium species ratios may be a place to lower the conversion of fuel nitrogen to fixed nitrogen. The addition of both NaOH and Na₂CO₃ lowered the amounts of fixed nitrogen measured. Therefore, higher concentrations of both of these in the liquor could be desirable. Likewise, the sulfur species seemed to slightly enhance the fuel nitrogen conversion to fixed nitrogen. While sulfur can not be eliminated in the process, lower concentrations or sulfur species in a more oxidized form, such as Na₂SO₄ rather than Na₂S, would be preferential to lower the fuel nitrogen conversion.

In terms of operating conditions, pyrolysis in a stagnant environment would be most preferable to reduce the conversion of the fuel nitrogen species to gaseous fixed nitrogen. Rapid mixing with O₂ is likely to increase fuel NO_x formation and therefore, char bed pyrolysis would be preferable to in-flight pyrolysis. Likewise, larger liquor

drop size could favor lower formation of gaseous fixed nitrogen species.

CONCLUSIONS

The following conclusions can be drawn from this work.

1. Black liquor nitrogen is primarily organic in nature. The content and composition of black liquor nitrogen is specific to both the tree species and pulping processes employed.
2. The nitrogen in black liquor is primarily associated with the lignin content further suggesting little to no nitrogen to be associated with the inorganics as salts.
3. Nitrogen is present in black liquor, allowing for multiple fuel nitrogen pathways to lead to the formation of NO_x .
4. Conversion of fuel nitrogen to fixed nitrogen during optimized combustion conditions (high temperatures with excess oxygen) is nitrogen-species specific. Nitrate tends to convert at equivalent rates regardless of the structure in which it is bound, while amine and heterocyclic compounds are more species specific.
5. The inorganic matrices in which the nitrogen species resides affect the conversion to fixed nitrogen. The effect appears to be both nitrogen-species specific as well as inorganic-species specific. The effect observed appears to be enhanced by increasing the concentration of the inorganic in the matrices.
6. During the slow pyrolysis of model fuel nitrogen compounds in both inert and oxidative environments, all fixed nitrogen was released by 400°C. Little to no enhancement of the fixed nitrogen release was observed for increased heating rates from 50°C/min to 150°C/min.
7. No effect of oxygen was observed for slow pyrolysis to 400°C in a dynamic flow environment. The greatest effect was observed for pyrolysis in stagnant conditions. A decrease of approximately 50% in the fixed nitrogen released was observed.
8. Possible NO_x control strategies for furnace operations include preferential use of char bed pyrolysis over in-flight pyrolysis and the use of larger liquor drop size. These suggestions likely favor lower formation of gaseous fixed nitrogen.

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