MINIMIZATION OF NO EMISSIONS FROM MULTI-BURNER COAL-FIRED BOILERS

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Department of Energy
University Coal Research Program

SEMI-ANNUAL REPORT

Grant No. DE-FG26-97FT97275--04

March 1999
through
September 1999

Program Overview

The focus of this program is to provide insight into the formation and minimization of NOx in multi-burner arrays, such as those that would be found in a typical utility boiler. Most detailed studies are performed in single-burner test facilities, and may not capture significant burner-to-burner interactions that could influence NOx emissions.

Our approach is to investigate such interactions by a combination of single and multiple burner experiments in a pilot-scale coal-fired test facility at the University of Utah, and by the use of computational combustion simulations to provide insight into the experimental results and to evaluate full-scale utility boilers. In addition, fundamental studies on nitrogen release from coal will be performed in support of the modeling effort. Improved submodels describing transformations of both volatile nitrogen species and char nitrogen species will be developed.

The program is broken into four main tasks:

1- Fundamental studies on nitrogen release from coal. These studies will be used to enhance the predictive capabilities of the combustion simulations. Studies focusing on secondary coal pyrolysis will be carried out at Brigham Young University, and studies focusing on char nitrogen will be performed at the University of Utah.

2- Comprehensive modeling of burner arrays. This task will be performed by Reaction Engineering International and the Unversity of Utah.

3- Pilot-scale optimization of multi-burner arrays. This task will be carried out by the University of Utah.

4- Technology transfer. This task involves coordination with utility consultants who will provide oversight of the research program.

FUNDAMENTAL STUDIES ON NITROGEN RELEASE FROM COAL

NITROGEN TRANSFORMATIONS DURING SECONDARY COAL PYROLYSIS

Introduction

Reduction of NO_x emission is an important environmental issue in pulverized coal combustion. The most cost-effective approach to NO_x reduction is air-staging which can also operate with additional down-stream techniques such as reburning [1]. Air staging promotes the conversion of NO_x precursors (HCN, NH_3, etc.) to N_2 by delaying the oxygen supply to the greatest extent when those nitrogen species are released during devolatilization. Such a delay gives the primary volatiles a chance to undergo secondary reactions, including tar cracking and soot formation. Secondary reactions of volatiles largely determine the fate of the ultimate NO_x production from pyrolysis, therefore a detailed investigation into the transformation of nitrogen species during secondary reactions and effects of soot on nitrogen release is critical for design and implementation of new pollution control strategies. Current nitrogen models (including the CPD model at BYU) only simulate the nitrogen release during primary pyrolysis, which happens at low temperatures. This project helps to build a nitrogen release model that accounts for secondary reactions and the effects of soot at temperatures relevant to industrial burners.

Objectives and Approach

The objectives of this project are:

(1) to effectively determine the mass release and soot/tar yield of four selected coals at different temperatures and residence times;

(2) to investigate the effects of such factors as coal rank, temperature, residence time on nitrogen release during secondary pyrolysis;

Accomplishments

Accomplishments for the past reporting period include the following:

1. Completion of a set of experiments in the Flat Flame Burner (FFB) that includes 4 coals, 4 temperatures and 4 residence times. These experiments provided char and tar/soot samples for elemental analysis and ICP analysis.

2. Completion of several test runs in the drop tube reactor (HPCP) that included 2 coals. Some minor changes were made to the HPCP, and temperature profiles were measured for two proposed conditions.

3. Accurate quantification of HCN, NH_3, light hydrocarbons and other significant N species in gas phase was performed using FTIR.

FTIR Analysis of N Species in Gas Phase

Quantification of gaseous N species (only HCN and NH_3) during pyrolysis was previously attempted using an HCN monitor. However, it was recently shown that the HCN monitor could not be used to accurately quantify HCN because of a huge drift of the data, resulting in standard deviations as high as 500%. NH_3 measurement was also shown to be unreliable using the HCN monitor. A high resolution Gas Chromatography had also been tested, however, the detection limit of the GC is only ~100 ppm.

A BOMEM MB155 FTIR coupled with a 9.75m multi-reflection gas cell was successfully used to perform on-line measurements of ppb-level HCN, NH_3, hydrocarbons and other significant species in the gas phase. Spectra were collected with a resolution of 1.00 cm^{-1} and spectral range of 500 cm^{-1}–4000 cm^{-1}. The pyrolysis gas from the sampling line was passed into the gas cell after passing glass filters. IR scans were made after the gas cell was purged for about 5 minutes. By using a liquid N_2-cooled MCT detector and 1-wavenumber resolution, the detection limit of the FTIR can be as low as 50 ppb for some gases (including NH_3, C_2H_4 and C_2H_2).

A CO flame (with a small amount of H_2) was used to perform the experiments, in order to minimize the amount of steam in the post-flame gases. Even with the large reduction in steam concentration, it is quite difficult to obtain IR measurements in a harsh environment containing 15% CO_2, 25% CO and small amount of water. All of these species are extremely strong IR absorbers, which can greatly interfere with the measurement of other weakly absorbing species. The data collected are also reliable and reproducible. Figure 1 shows sample spectra of HCN and NH_3 from coal pyrolysis in the CO flame.

Future Plans

Future plans include completing a series of pyrolysis experiments on selected coals in the FFB. Analysis of data from these experiments will permit the examination of nitrogen release behavior during the second stage of coal pyrolysis. The effect of soot on nitrogen transformation is also an indispensable part in this project.

References

1. Man, K. C., Russell, N. V. and Gibbins, J. R., A Kinetic Study of Secondary Volatile Nitrogen Release From Coal, ACS Div. of Fuel Chemistry Preprints, 43:3, 1138-1142 (1998).

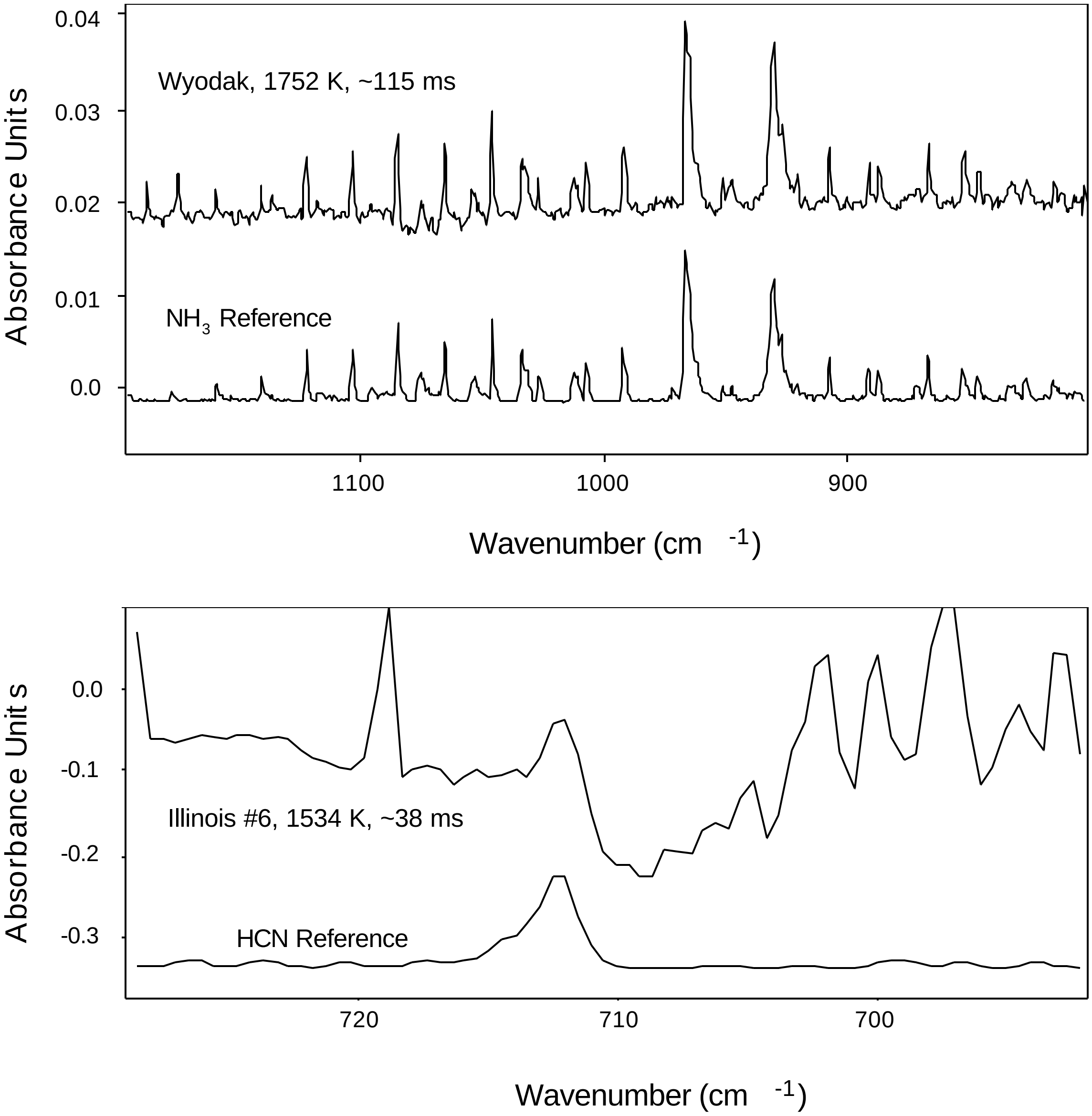

Figure 1. Comparison of measured and reference spectra for HCN and NH$_3$.

Char Nitrogen Studies: Models for the Production of NO During Char Combustion

In order to increase and understand the capabilities of the Simplified Single Particle Model (SSPM) described in the report March 1998 and expanded in September 1999, a review of the existence single particle model existing in the literature was performed. This review allowed to distinguish the critical points were the SSPM has to be improved. It also suggested topics in which further research should focus in order to strength the capabilities of the SSPM on predicting the amount of char-N converted to NO.

1. LITERATURE REVIEW.

One way to obtain greater insight on char-nitrogen conversion to NO during coal combustion is to model its production from a single char particle. However, there are several characteristics of the physics and chemistry of this system that remain to be defined,[1-4] making it difficult to develop a model. Despite such difficulties, different models[2,5-9] have been proposed to predict the generation of NO from a single char particle. As models, they employed engineering approximations to address uncertainties in the basic mechanisms and kinetics. This section describes these assumptions and attempts to define under what conditions they are valid.

Table 1 presents the set of reactions used by different models. The assumptions concerning the most important reactions of these systems are summarized next.

- **Carbon oxidation**

The carbon in the char is considered to react heterogeneously with oxygen to produce CO in a one-step reaction in most of the models. Only de Soete et al[7] considered a three-step heterogeneous reaction system in which CO and CO_2 are produced heterogeneously. The homogeneous oxidation of CO to CO_2 was also considered by two models.[6,8] Although there is experimental evidence10 of some direct CO_2 heterogeneous production, the main path at combustion temperatures is the heterogeneous production of CO during char oxidation.[11] It is also well known that most of the CO_2 produced during combustion comes from the homogeneous oxidation of CO. However the possibility of the occurrence of this reaction inside the pores of the char where Knudsen diffusivity may prevail is low. Therefore, only considering the heterogeneous production of CO during char oxidation may be a good approximation.

- **HCN formation and destruction**

New experimental evidence[12] suggested the importance of HCN as an intermediate in the production of NO. This observation justifies the presence of reactions for its formation and reduction in Visona and Stanmore's[9] model. These authors not only considered NO formation from HCN, but also its influence in the reduction of NO. The lack of expressions that predict the production of HCN from char oxidation forced these authors to use an empirically-defined parameter that determines the amount of char-N that evolves as NO or HCN.

The inclusion of HCN as an intermediate in this reaction system may be important at: *1)* the temperatures typical of fluidized bed reactors; and *2)* if the prediction of N_2O production is the objective. This was the case in the Winter et al.[12] study. Nevertheless, the rapid oxidation of

HCN to NO, as described for instance in the Jones et al. experiment13 in which HCN can only be detected if the gas analysis probe is placed immediately on the top of the char sample, may justify neglecting HCN production during pulverized coal combustion, where N_2O production is negligible.

- **NO formation**

All the models consider the formation of NO from the heterogeneous oxidation of the char-N. Goel et al[6] and de Soete et al[7] also defined the formation of a heterogeneous complex (hypothesized to be –CNO) that is responsible for N_2O formation.

As stated above, the importance of including –CNO (or HCN) as intermediates for NO production during char combustion decreases at pulverized combustion conditions where N_2O, either because it is not formed or because it is reduced so rapidly, is not detected as a main product. When modeling combustion reactions in fluidized beds, approximations such as those of Goel et al[6] and de Soete et al[7] with –CNO, or that of Visona and Stanmore[9] with HCN as intermediate may be required. But the simple heterogeneous formation of NO from char-N neglecting any intermediates may be an adequate approximation at pulverized coal combustion conditions. Obviously, the development of further comprehensive models for this reacting system should pursue a good representation of results at high and low temperatures.

It is also important to consider the rate expression used to represent NO production from char-N oxidation. The most common approach[5,8,9] is to consider that it is proportional to the rate of carbon oxidation from the char, the proportionality constant being the ratio of nitrogen/carbon atoms ($^{N}\!/_{C}$) in the parent char; i.e.,

$$R_{NO} = \left({}^{N}\!/_{C} \right)(-R_C) \qquad \text{E 1}$$

Where R_C is the rate of carbon consumption and R_{NO} represents the rate of NO formation from char-N oxidation. This approximation, although realistic, is not exact as shown by the data on fifteen coals analyzed by Baxter et al.[14] These authors studied the evolution of nitrogen containing compounds from coals during coal devolatilization and char oxidation and concluded that nitrogen evolution is not proportional to the coal burnout rate. Ashman et al[15] observed that the molar N/C ratio of the product gases (normalized by the N/C ratio of the char) as a function of char conversion remained as 1 at T = 1173 K, whereas it varied from 0.3 to 1.8 at T = 873K. They obtained the results during char oxidation in a 2% O_2/He mixture carried out in a TGA. Ashman et al's[15] results suggest that at higher temperatures there is no selectivity between nitrogen and carbon loss due to oxidation. A similar result was obtained by Song et al[16] at temperatures ranging from 1250 to 1750 K when burning Montana lignite char at oxygen partial pressures of 0.2 and 0.4 atm.

Figure 1 presents the results of Ashman et al[15] and an example of those of Baxter et al[14] for one coal. Both are presented as the ratio of N/C in the gaseous products of combustion to that of the parent char. Values above one in this ratio signify that nitrogen is preferentially released from the char during oxidation while values less than one imply that the nitrogen accumulates in the char. As observed in Figure 1, the Baxter et al[14] study detected that at the onset of the char oxidation there is preferential release of nitrogen. The authors consider that in the early stages of combustion, nitrogen-containing aromatic structures are less stable thermally and may be more susceptible to heterogeneous oxidative attack. The temperature range of Baxter et al's[14] experiments was between 1500 – 2000 K.[17] In contrast, Ashman et al's[15] experiment at 873 K shows accumulation of nitrogen atoms in the char during combustion. These results were confirmed by elemental analysis of the residual char. For Ashman et al, [15] the growing relative amount of pyridinic N and the reduction of pyrrolic N during char oxidation, may be responsible for the accumulation of nitrogen in the char since pyrrolic rings may be preferential oxidized than pyridinic rings. Although the Ashman et al[15] results are in contradiction to the results by Baxter et al,[14] the comparison is obscured by the differences in temperature between both experiments.

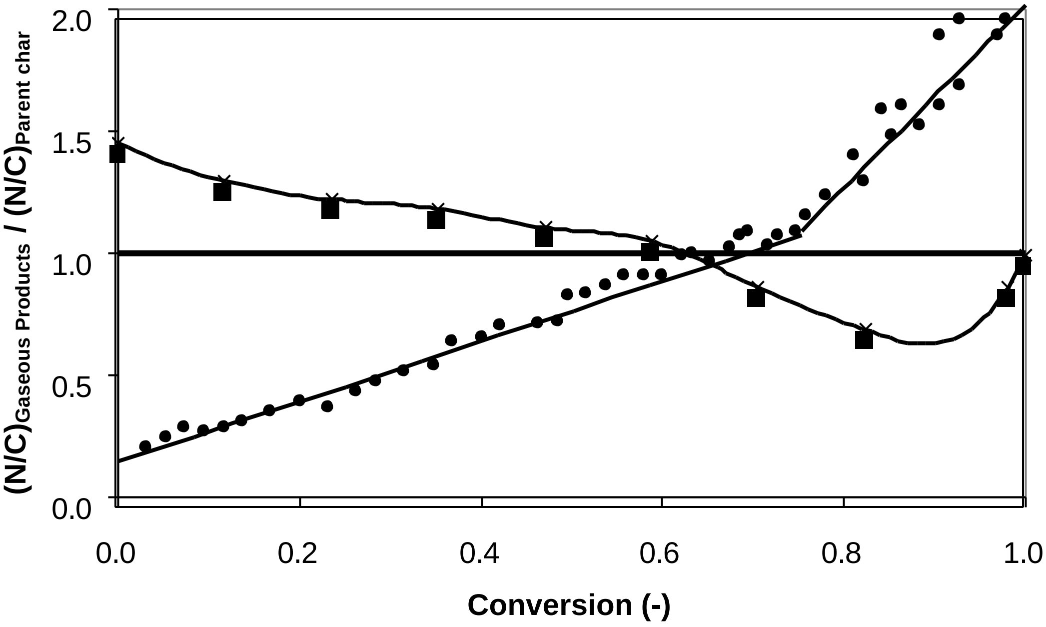

Figure 1. Molar N/C ratio of the product gases (normalized by the N/C ratio of the parent char) as a function of char conversion. Squares: Data adapted from Baxter et al[14] for North Dakota Lignite. **Circles:** Data from Ashman et al[15] for HVB coal char oxidized at 873 K

A thought experiment would suggest that when a carbonaceous solid is consumed all elements will be released in proportion to their concentration. Exception will be those elements, such as inorganic elements, that accumulate because they are not vaporized. The two conditions under which nitrogen will not be released in proportion to carbon are those under which nitrogen is preferentially released by pyrolytic reactions (high temperatures) or when the products such as NO are adsorbed (low temperatures).

Obviously at high enough temperatures to burn at diffusion limited rate, nitrogen and char will be consumed at the same rate. The impact of departures from this limit will be examined later.

- **NO reduction**

In their pioneering study, Wendt and Schulze8 only considered the homogeneous reduction of NO, but they didn't specify any mechanism. As pointed out previously, NO is mainly heterogeneously reduced on the char surface as in three of the models presented in Table 1. The additional reduction of NO by CO catalyzed by char surface (R 1), is also considered by Shimizu et al[5] and Goel et al.[6]

$$NO + CO \rightarrow \tfrac{1}{2} N_2 + CO_2 \text{ (surface catalyzed)} \qquad \text{R 1}$$

Visona and Stanmore[9] also considered the homogeneous reduction of NO with HCN.

The models that considered the heterogeneous reduction of NO on char defined the reaction as first order with respect to NO. The value of the kinetic constants used varied for each model. Visona and Stanmore[9] compared the kinetic constants for the reduction of NO on char surface reported by de Soete,[18] Levy et al,[19] Song et al[20] and Chan et al[21] and recommended Chan's et al[21] as the one that best fitted their experimental data. Goel et al[6] applied a least squares optimization method to experimental data in order to evaluate the thirteen constants used in their kinetic model. de Soete et al[7] also used experimental data to evaluate the 25 constants associated with their detailed model. de Soete et al's[7] experiments also included transient analysis of the reaction system. All constants were dependent on the type of char analyzed.

The rate constant for the destruction of NO with CO catalyzed by char (R 1) was determined from the same least square optimization technique by Goel et al.[6] Shimizu et al[5] on the other hand used Chan's et al[21] expression for NO reduction in the presence of CO.

The wide range of approaches to the NO-char reaction is an indication of the uncertainty on the kinetics of the reaction and the best way to model it. The influence of the kinetic rate for NO reduction on char will be considered later.

Table 1. Comparison of some single particle models used in the prediction of NOx emissions
Set of reactions considered

Model	**Wendt and Schulze**[8]	**Shimizu et al**[5]	**Goel et al**[6]	**Visona and Stanmore**[9]
C oxid.	$C + \frac{1}{2}O_2 \xrightarrow{k_1} CO$	$C + \frac{1}{2}O_2 \longrightarrow CO$	$(-C) + O_2 \xrightarrow{k_{O_2}} CO + -O$	$(-C) + O_2 \xrightarrow{k_{O_2}} CO$
CO oxid.	$CO + \frac{1}{2}O_2 \xrightarrow{k_4} CO_2$		$CO + \frac{1}{2}O_2 \xrightarrow{k_{CO}} CO_2$	--------
HCN gen.	--------		--------	$-CN \longrightarrow HC$
HCN oxid.	--------		--------	$HCN + O_2 \xrightarrow{k_{HCN}}$ $HCN + NO \xrightarrow{k_{HCN-NO}}$
NO gen.	$Char - N + \frac{1}{2}O_2 \xrightarrow{k_2} NO$	$Char - N + \frac{1}{2}O_2 \longrightarrow NO$	$-CN + O_2 \xrightarrow{k_0} -CNO + -O$ $-CNO \xrightarrow{k_1} NO + -C$	$\frac{1}{2}O_2 + -CN \longrightarrow$ $HCN + O_2 \xrightarrow{k_{HCN}}$
NO reduct.	$NO + \bullet\bullet\bullet \xrightarrow{k_3} N_2$	$NO + CO \longrightarrow \frac{1}{2}N_2 + CO_2$	$NO + -C \xrightarrow{k_{NO}} \frac{1}{2}N_2 + -CO$ $NO + CO \xrightarrow{k_{NO-CO}} \frac{1}{2}N_2 + CO_2$	$HCN + NO \xrightarrow{k_{HCN-NO}}$ $NO + -C \xrightarrow{k_{NO}}$
N_2O gen.	--------		$-CNO + NO \xrightarrow{k_2} N_2O + -C$	--------
N_2O reduct.	--------		$N_2O + -C \xrightarrow{k_{N_2O}} N_2 + -CO$	--------

C*: free carbon site**

2. INFLUENCE OF KINETIC PARAMETERS ON THE AMOUNT OF CHAR-N CONVERTED TO NO

In order to understand the influence of the rate expression for the reduction of NO on the char surface on the final prediction of char-N conversion to NO, the simplified single particle model (SSPM), similar to those of Table 1 and described in previous reports was used. Basically, the model considers the heterogeneous production of CO from char, the heterogeneous reduction of NO on the char surface and the direct production of NO from char-N oxidation. E 2 and E 3 present the rate expressions.

$$R^{v}_{O_2} = -k_{O_2} C_{O_2} \qquad \text{E 2}$$

$$R^{v}_{NO} = 2\left({}^{N}\!/_{C}\right) k_{O_2} C_{O_2} - k_{NO} C_{NO} \qquad \text{E 3}$$

Where R^{v}_{i}, k_i and C_i are the volumetric rate of reaction, the rate constant and the concentration of species *i* respectively. The main assumptions of this model are: *1)* all char-N goes either to NO or N_2 or in other words, N_2O and HCN production are neglected; *2)* the influence of CO on the reduction of NO on the char surface is also neglected; and *3)* all reactions are considered to be first order. These assumptions restrict the applicability of the model only to specific cases. For instance, assumption *1)* makes the model applicable only at high temperatures (>1400 K), where N_2O is not a product of char oxidation.

This model may provide understanding of the influence of the rate of NO reduction on char, the rate of carbon oxidation and the nature of nitrogen release during char oxidation on the conversion of char-N to NO. This understanding may suggest opportunities for further research in this area and for strategies for NO control.

- **Reduction of NO on char surface.**

Figure 2 presents a summary of first order rate constants for the reaction of NO reduction in the high temperature regime. The continuous lines represent the results from expression E 4 and its high and low limits calculated by multiplying the rate given by by 10 and 0.1 respectively.

$$k = 5.5 \text{ x } 10^6 \exp(-15939/T)\,[\mathrm{g_{NO} m^{-2} h^{-1} atm_{NO}^{-1}}] \qquad \text{E 4}$$

E 4 was developed by Aarna and Suuberg's[3] from a least square average of results from twenty-four different carbonaceous materials and different research groups and claimed that it represents the experimental data within one order of magnitude. The dashed lines represent the kinetic values reported by Guo and Hecker[22] for two coals (North Dakota Lingnite and Pocahontas). These two coals were chosen because they were the highest and lowest kinetics in Guo and Hecker's[22] experiments. It is clear that expression E 4 represents within one order of magnitude the kinetics presented in Figure 2. Other kinetics, (de Soete,[18] Levy et al,[19] Song et al[20] and Chan et al[21]) were also found to be within the limits of Aarna and Suuberg's[3] expression.

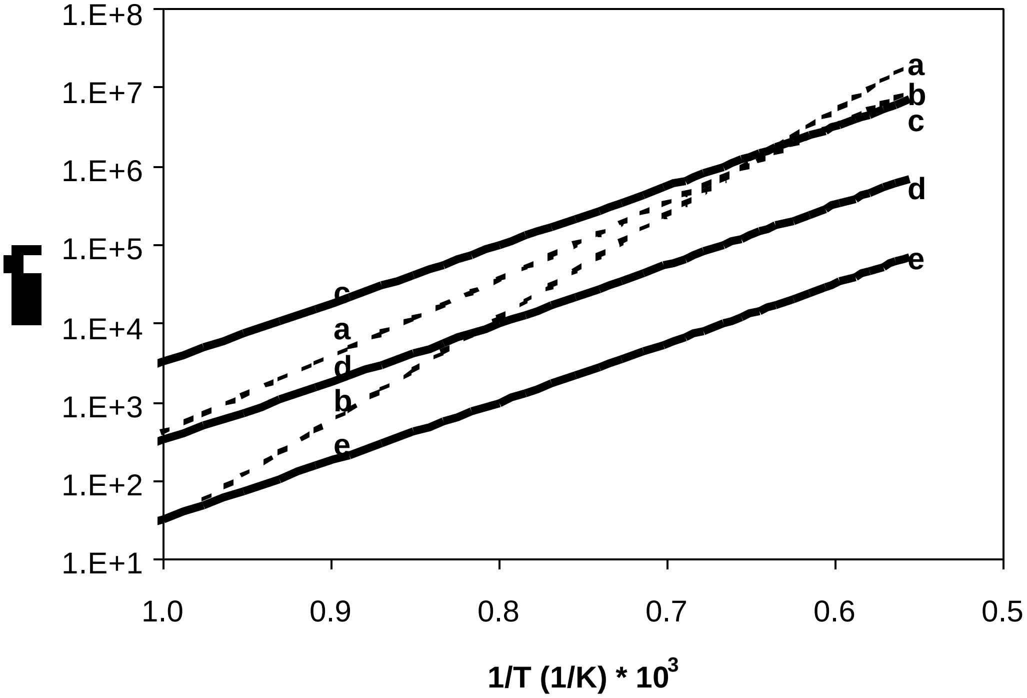

Figure 2. First order rate constants for the reaction of pure NO with coal chars. Char surface area = 530 m²/g. P_{NO} = 101325 Pa. r_p =1250 kg/m³. a. Guo and Hecker[22] (Pocahontas)**; b.** Guo and Hecker[22] (NDL); **c.** 10*Aarna and Suuberg[3]**; d.** Aarna and Suuberg[3]**; e. 0.1***Aarna and Suuberg[3]

Figure 3 presents the predictions of char-N conversion to NO from the SSPM. Char properties and experimental conditions were chosen to approximate those of Song et al.[23] The kinetic rate of Smith[24] was used for the carbon-O_2 reaction.

The constants for the five kinetic rates presented in Figure 2 were used in the SSPM. The data show an increase in the conversion of char-N to NO as the temperature is reduced from 1800 K to 1000 K. Although a similar trend is reported by Ashman et al,[15] the results should be interpreted as qualitative, especially at temperatures below 1400 K where the production of N_2O begins to be important. In fact, de Soete[**18**] and de Soete et al[7] present the opposite trend, however their experiments were in the a lower range of temperature (800 to 1100 K) in which N_2O production is considerable. At high temperatures, the dependence of conversion with temperature decreases. This is in accordance with the results of Pershing and Wendt[25] for char combustion at pulverized coal conditions. These authors concluded that the fuel nitrogen conversion to NO from char burned in a pulverized combustor was only a weak function of flame temperature. This suggests, as expected, that the predictions of the SSPM may be reasonable at high temperatures.

As in Figure 2, the continuous lines represent Aarna and Suuberg's[3] generalized expression for NO reduction on the char surface and the limits within one order of magnitude. The dashed lines are the predictions according to Guo and Hecker's[22] results.

At the high temperatures in which the SPPM may predict more realistically the results, the amount of char-N converted to NO varied from 0.98 for the lowest value of k_{NO} to 0.24 for the highest value. This shows the importance of the kinetics of NO destruction on char surface on the final prediction of char-N conversion to NO.

Finally, curves f and g show the predictions of the SSPM when the NO concentration surrounding the particle is increased to 750 ppm. The expression by Aarna and Suuberg,[3] and the kinetics of Guo and Hecker[22] for the Pocahontas coal were the equations used for the reduction of NO on a char. A considerable reduction on the conversion of char-N to NO is predicted. In fact, at 1800 K the SSPM predicts a negative value if the kinetics of Guo and Hecker[22] is used. This agrees with Spinti's results[26] that showed a reduction on char-N conversion to NO as the NO bulk concentration increases. Higher NO concentration increases the rate of NO destruction inside the particle. A negative value of char-N conversion to NO may be understood thus as a rate of destruction of NO by the char which exceeds the nitrogen fed in the char.

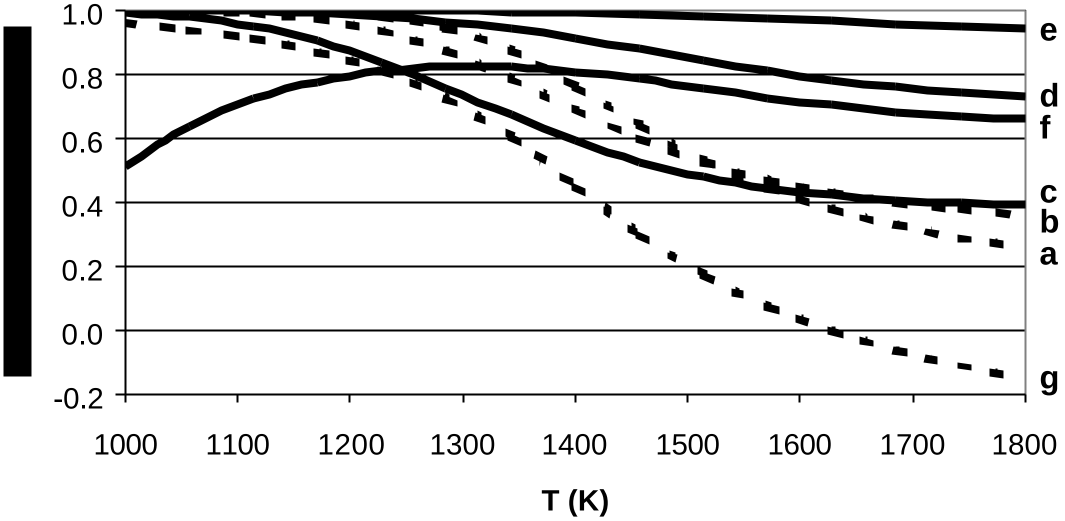

Figure 3. Char-N conversion to NO as predicted by the SSPM.
Particle size = 38µm. O_2 concentration around the particle= 0.21; NO = 0 (except for cases f and g). Captions as in Figure 2. f. Aarna and Suuberg[3] NO = 750 ppm. **g.** Guo and Hecker[22] (Pocahontas) NO = 750 ppm

Figure 3 illustrates not only the importance of the selection of adequate kinetic rates for NO reduction, but also the significance of selecting the right kinetic mechanism. The simple mechanism of the SSPM is not accurate enough to predict the results at lower temperatures were HCN and N_2O become important intermediates.

- **Carbon-oxygen reaction.**

Figure 4 presents the influence of the rate of carbon reaction with O_2. The base cases are the results obtained when the carbon oxidation kinetics of Smith[24] are used. The transformation of the conversion of char-N to NO when the oxidation kinetics is varied within one order of magnitude was studied for the rate expressions of Aarna and Suuberg[3] and Guo and Hecker.[22] The faster the reaction of carbon with oxygen, the higher the conversion of char-N to NO since the rapid consumption of the char will reduce the possibilities of NO reduction on the surface of the char. Figure 4 also underscores the importance of the model used for the prediction of the coal oxidation.

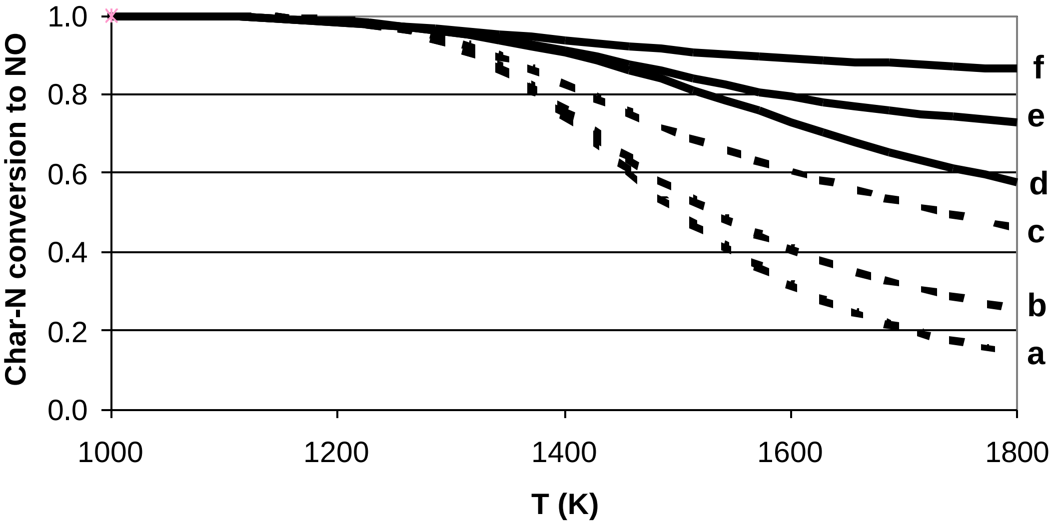

Figure 4. Char-N conversion to NO as predicted by the SSPM. Particle size = 38µm. O_2 concentration around the particle= 0.21; NO = 0 Continuous lines: NO kinetics from Aarna and Suuberg;[3] Dashed lines: Kinetics of Guo and Hecker[22] for Pocahontas. For a. and d., $k_{O_2} = 0.1 * k_{O_2}$ by Smith.[24] b. and e. with k_{O_2} from Smith.[24] And c. and f. with $k_{O_2} = 10 * k_{O_2}$ by Smith.[24]

- **Rate of nitrogen release during char oxidation**

As discussed before, most of the models for char-N conversion to NO considered that the rate of NO formation is proportional to the ratio N/C of the parent char. However, Figure 1 presented two different experimental results that show that the ratio N/C varies during char combustion.

To understand the influence of this variation on the conversion of char-N to NO, empirical expressions of ${}^{N}\!/_{C}$ as a function of char conversion were derived from Figure 1 and applied to the SSPM. The kinetics of Aarna and Suuberg[3] for char-N oxidation and the one of Smith[24] for the carbon – oxygen reaction were used in all the simulations.

Figure 5 presents the results. Lines **b** and **c** are SSPM predictions when a constant value of ${}^{N}\!/_{C}$ is used for Baxter et al[14] and Ashman et al[15] chars. The different final prediction of char-N conversion to NO is due to the different char composition of both experiments. Lines **a** and **d** presents the results when a variable value of ${}^{N}\!/_{C}$ is used. Although the experiment of Ashman et al[15] was carried out at 873 K, the results of Figure 5 are at 1750 K for both expressions for ${}^{N}\!/_{C}$ to allow comparison.

There is little difference in the final prediction of char-N conversion to NO when the empirical correlation for ${}^{N}\!/_{C}$ obtained from the Baxter et al[14] experiments is used (lines **a** and **b**). The reason for this is that Baxter et al[14] (Figure 1) found that most of the N was released at the beginning of char oxidation. At these stages of the reaction, the particle has enough surface area for reducing the NO being formed. Therefore, although line **a** exceeds line **b** at the low values of conversion, the difference between both lines is less than what is expected when Figure 1 is considered. At high conversion, Baxter et al[14] observed that the release of N was less than that predicted according to the value of ${}^{N}\!/_{C}$ for the parent char. Therefore it may be expected that the production of NO is slow and this phenomenon is observed in Figure 5. The net sum of these two effects is that the final conversion of char-N to NO is almost the same with variable and constant value of ${}^{N}\!/_{C}$.

On the contrary, when the empirical expression of Ashman et al[15] is used, the final conversion of char-N to NO differs considerably from the one obtained when a constant value of $^{N}\!/_{C}$ is used. As observed in Figure 1, Ashman et al[15] found that nitrogen accumulated in the char during combustion. Therefore, during the first stages of the oxidation when there is large carbon area for the reduction of NO on char surface, the production of NO is low. Conversely, at high conversions, where the capacity of NO reduction by the char is low, the release of NO is higher, and thus the conversion of char-N to NO is higher.

The results of the SSPM suggest that the final conversion of char-N to NO may be influenced by the time when N is released during the oxidation of the char. The retention of N in the char may increase the amount char-N converted to NO whereas a premature release of N may reduce it.

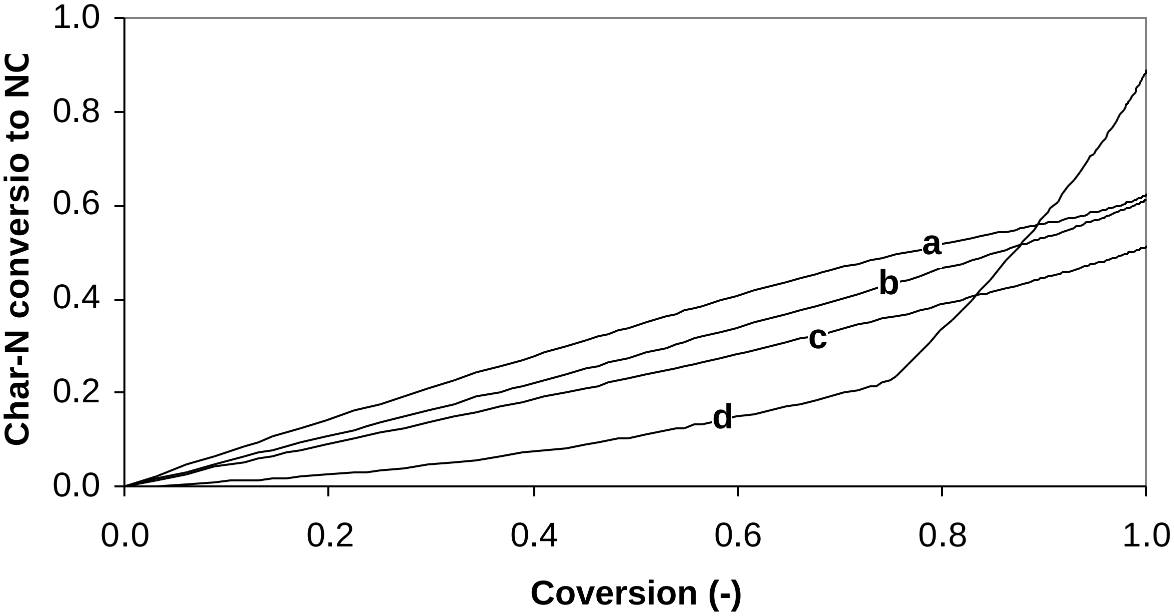

Figure 5. Prediction of char-N conversion to NO as a function char conversion according to the SSPM. Particle temperature = 1750°K. The influence of the variation

of $^{N}\!/_{C}$ during combustion is analyzed. Baxter et al:[14] **a.** Variable $^{N}\!/_{C}$ **; b.** Constant $^{N}\!/_{C}$ **.**
Ashman et al:[15] **c.** Constant $^{N}\!/_{C}$ **; d.** Variable $^{N}\!/_{C}$ **.**

3. IMPLICATIONS FOR COAL-FIRED UTILITY BOILERS

Since the combustion behavior of single particles can vary considerably within coal-fired utility boilers, it is difficult to use a single particle model to describe overall behavior. To overcome this difficulty, computational fluid dynamic (CFD) codes have been used extensively when modeling combustion in coal-fired utility boilers. Particularly in the study of NO production, various authors have tried to use computer-modeling codes for the prediction of NO emissions during coal combustion.[27-40] Agreement between experimental data and model predictions varies; however, most are capable of prediction of NO concentration trends, even if exact values at specific points are sometimes not predicted accurately.

While modeling NO production during pulverized coal combustion, the most common approach is to develop the NO production routine as a post-processing model for the main comprehensive model. This post-processor uses the temperature, flow-field and concentration results obtained from the main combustion model calculations, and the NO production model is thus decoupled from these calculations. This is a reasonable approach since due to their low concentration, the nitrogen-containing species have a negligible influence on the mass, heat and momentum balances of the complete furnace.

The most common approach for modeling the conversion of char-N to NO is the one proposed by Smith et al.[41] According to this model, the release of N from the char is proportional to the mass consumption during char combustion. All fuel-N is converted to HCN, which is then either oxidized to NO or reduced to N_2 according to the kinetic rates of de Soete.[42] This approach is described by the dashed lines in Figure 6, and is used extensively in CFD simulations.[27-31,38] Variations of this approach include a fixed efficiency factor for the direct conversion of char-N to NO_x, This factor may be zero[35] or a value between zero and one obtained either empirically[32,34,37] or by considering the reduction of NO with char or CO36,43 More refined approaches allow for the separate formation and destruction reactions as described by Jones et al[44] and in the following paragraphs**.** Some others authors not only consider that the nitrogen is released as HCN, but also as NH_3[40,45] depending on its functional form in the coal. These approximations have been sufficient for predicting with reasonable accuracy the total NO production from coal combustion. However, as the level of NO production in the boilers is reduced due to more stringent regulations, the relative importance of the NO produced from the char increases, and it may be necessary to use models that approximate in a more accurate way the physics in this system. Examples of these are the single particle models described previously. One example of the improvements obtained when a more accurate char-N description is used was presented by Eddings et al.[37] These authors extended the model by Smith et al[41] by considering volatile-N and char-N as two different streams (continuous lines in Figure 6). This variation in the model improved code predictions as observed in Figure 7. By considering nitrogen evolution from the char, independent from nitrogen evolution from volatiles, Eddings et al[37] considerably reduced the over-prediction of NO for all the coals they analyzed (Figure 7). Visona and Stanmore[40] also compared different approaches for the model of char-N conversion to NO while modeling a swirling pulverized coal flame. These authors did not find an optimum approach, and concluded that the principal limitation in their model were the uncertainties associated with the model for char-N to NO conversion.

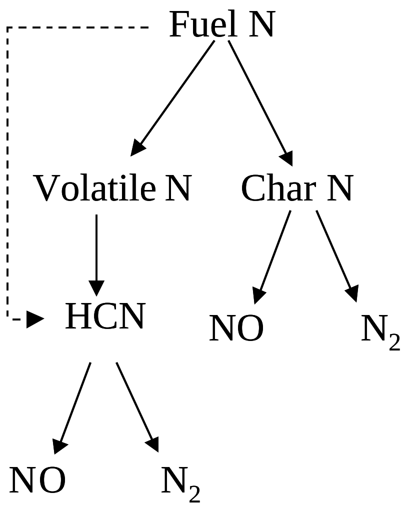

Figure 6. Suggested simplifications used in CFD for approximating the fuel-N that is transformed to NO. Dashed lines: Traditional model by Smith et al.[41] Continuous lines: Model by Eddings et al.[37] h **: From experimental results or models.** a **:Fixed value.**

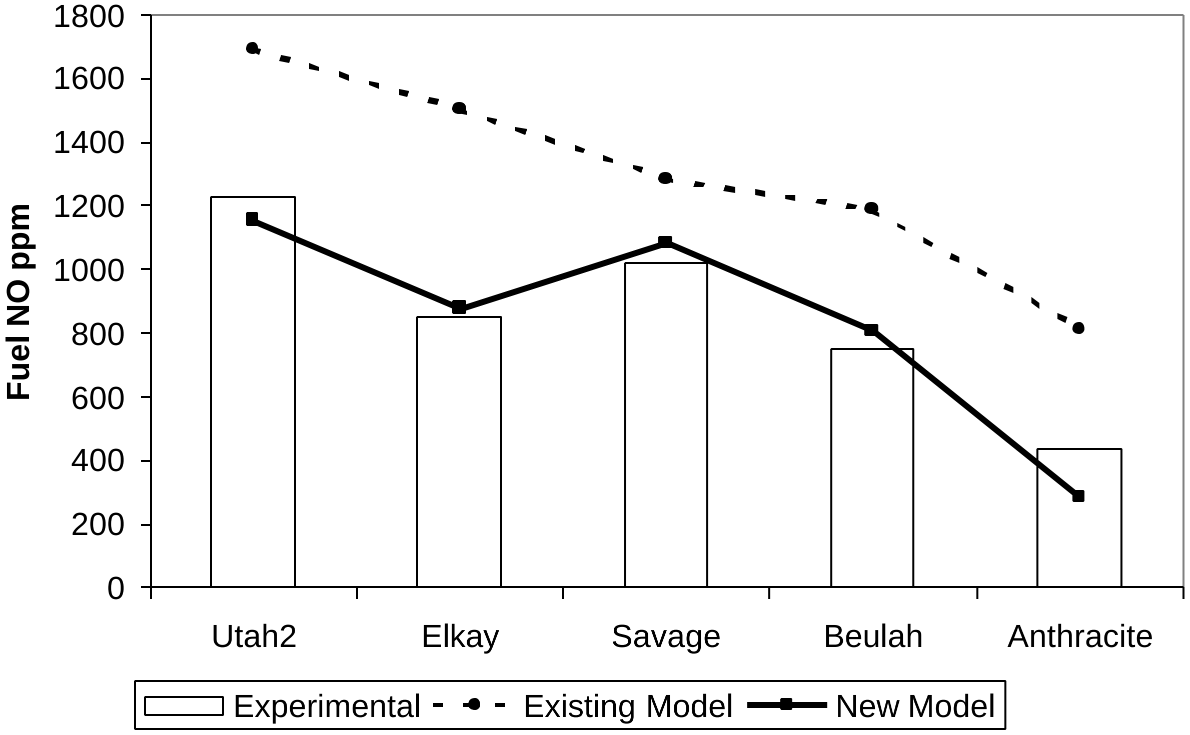

Figure 7. Comparisons of exhaust NO values with model predictions during pulverized coal combustion.[37]

Another attempt to apply a single particle model for the prediction of char-N evolution to NO was presented by Sarofim et al.[2] These authors applied the SSPM previously described as a post-processor for the prediction of NO formation from coal particle trajectories in a 500 MW utility boiler. The boiler is an opposed-wall-fired pulverized coal unit that had undergone a low NOx burner retrofit. The burner retrofit reduced the measured NOx emissions at the plant from approximately 800 ppm to below 400 ppm. The SSPM model was used to investigate char N conversion behavior in a full-scale utility boiler both before and after the low NOx burner retrofit, where the environment experienced by burning char particles were quite different. The pre-retrofit burning environment was predominantly oxidative; whereas the post-retrofit environment was predominantly reducing. The SSPM model was coupled with *GLACIER*, a reacting computational fluid dynamics (CFD) code developed for modeling three-dimensional, reacting two-phase flows using a Lagrangian particle cloud tracking technique.

With the input data from the CFD code, the SSPM was able to predict the cumulative conversion of char-N to NO, F_{NO}. The value of F_{NO} can be negative if NO production inside the particle is smaller than the NO consumption by the reduction reaction, i.e. E 3 < 0. Sarofim et al[2] compared the results for one boiler before and after the implementation of a NO_x control strategy (low NO_x burners with over-fire air). The information obtained from the CFD code corresponded to a total of 3456 different particle cloud trajectories. For each trajectory, the particle size, the oxygen and NO bulk concentration and the particle temperature vs. residence time were known. The SSPM predicted an individual value of the conversion of char-N to NO,

F_{Noi}, for each trajectory. Figure 8 presents the predicted values of F_{NO} against cumulative mass particle weight. Two characteristics of Figure 8 should be highlighted: *1)* the wide range of values predicted for F_{NO} (–3% to 100%); and *2)* the results for both cases, pre and post-retrofit, are very similar. The first point is not surprising, considering the variable atmospheres to which different chars may be exposed in a large utility boiler. Particles submitted to reducing atmosphere, i.e. fuel-rich pockets, may act as reducing agents. Particles in contact with oxygen, will be rapidly oxidized and the possibility for NO reduction will be low. However, the similarity of the predictions of F_{NO} for both cases was unexpected. Sarofim et al[2] proposed that this was the result of a trade-off of two different effects. Table 2 presents mass average values of the concentration of NO, O_2 and particle temperature during the trajectories of all char clouds, for both cases. As expected, the average NO concentration is lower for the post-Retrofit case. This lower concentration should reduce the capability of the char for reducing NO (see Figure 3). However, the technique used for NO reduction in the furnace, not only reduced the local concentration of NO, but also decreased local O_2 concentration. A reduction in the O_2 concentration will reduce the rate of carbon oxidation, and as shown in Figure 4, this will reduce the amount of coal nitrogen transformed into NO. The predicted value for the mass average of F_{NO} is close to previous results reported by Pershing and Wendt,[25] and Chen et al,[46] (10 – 20 %) for similar conditions, providing some confidence in the calculations.

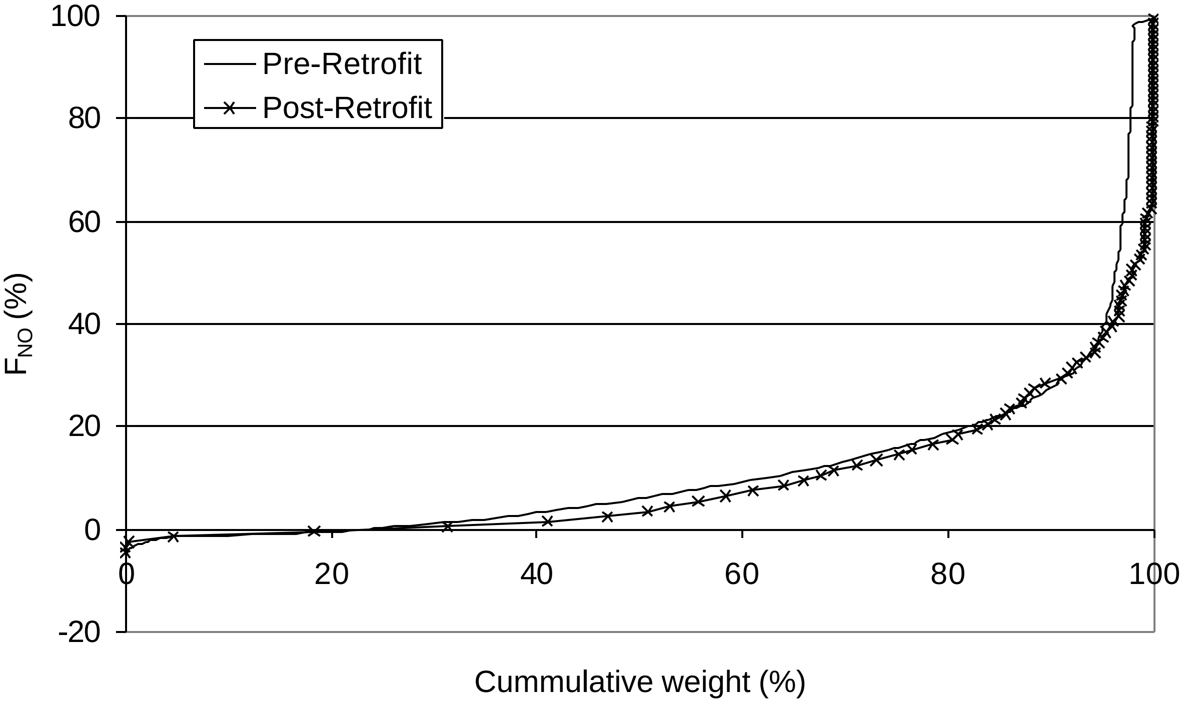

Figure 8. Distribution of char-N conversion to NO, F_{NO}, as predicted by a single particle model for two different boilers. From Sarofim et al[2]

Table 2 Summary of predictions of the SSPM for two different boilers, Pre and Post-low NO strategy. After Sarofim et al.[3]

Case	Pre-Low NO_x	Post-Low NO_x	Pre/Post
Number of trajectories	1536	1920	-
Average NO_x (ppm) along char cloud trajectories, normalized by mass	475	327	1.5
Average O_2 (%) along char cloud trajectories, normalized by mass	5.8	1.5	3.9
F_{NO} (%) (average) (wt)	13.2	11.1	-
Temperature during char trajectory, normalized by mass (K)	1442	1515	0.95
Predicted Exit NO concentrations (ppm)	803	351	2.3

Regardless of the numerous assumptions associated in Sarofim et al's simulation, their results illustrate the complexity of this system and demonstrate the need to include the effects of all the main combustion parameters into char NO calculations.

In the above calculations the NO concenration field was calculated using a mean char nitrogen conversion efficiency. The NO concentration should be calculated interactively with the calculation of char nitrogen conversion. Procedures for coupling the homoegeneous and heterogeneous kinetics include the use of Zone Models as described in reference [47].

Pilot-Scale Studies: Preparations for Multiburner Firing

Four 1.5 MMBtu/hr dual swirl block burners (Figure 1) were designed to fit on the L1500 Furnace at the University of Utah. This burner design is patterned after an existing 5 MMBtu/hr burner. Each burner has the ability to independently vary the swirl of the secondary and tertiary air from a swirl number (Ratio of tangential momentum to axial momentum) of 0-2 with the use of swirl blocks. The design parameters are described in table 1.

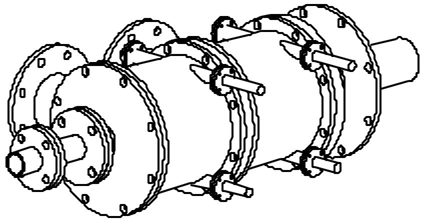

Figure 9. Burner Drawing

Nominal Firing Rate	**1.5**	**MMBtu/hr**
Primary Air Stoichiometric Ratio	**0.15**	
Primary Air Velocity	**80**	**ft/sec**
Primary Air Temperature	**150**	**F**
Secondary Air/Tertiary Air Ratio	**33%/66%**	
Secondary Air Swirl Numbers	**0-2**	
Secondary Air Velocity	**85**	**ft/sec**
Secondary Air Temperature	**600**	**F**
Tertiary Air Swirl Numbers	**0-2**	
Tertiary Air Velocity	**115**	**ft/sec**

Table 3. Burner Design Parameters

Each register contains a set of stationary and a set of moveable blocks. Figures 2 and 3 show the air can be shifted from an axial direction (no swirl) to a tangential direction (full swirl) by moving the moveable blocks.

At any given time, three burners (top, middle, and bottom) will be in operation. By choosing three burners, the middle burner will be shielded from wall effects and thus give a better burner to burner interaction. Burner wall effects can be determined using the outer two burners.

In an effort to determine the effect of swirl direction, three burners were designed with a clockwise swirl and the fourth burner was designed with a counter-clockwise swirl. The opposite swirl burner can be installed in any of the three positions.

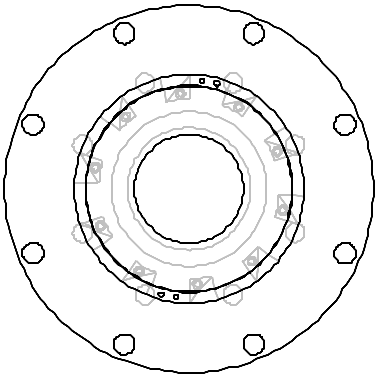

Figure 10. Burner swirl blocks in the no swirl position.

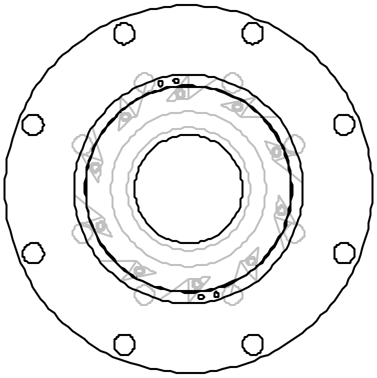

Figure 11. Burner swirl blocks in the full swirl position.

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