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

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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

Coal contines to be one of the principal energy sources for electric power generation in the United States. One of the biggest environmental challenges involved with coal utilization is the reduction of nitrogen oxides (NO_x) formed during coal combustion. The most economical method of NO_x abatement in coal combustion is through burner modification. Air-staging techniques have been widely used in the development of low-NO_x pulverized coal burners, promoting the conversion of NO_x to N_2 by delaying the mixing in the fuel-rich zone near the burner inlet. Previous studies have looked at the mechanisms of NO_x evolution at relatively low temperatures where primary pyrolysis is dominant, but data published for secondary pyrolysis in the pulverized coal furnace are scarce. In this project, the nitrogen evolution behavior during secondary coal pyrolysis will be explored. The end result will be a complete model of nitrogen evolution and NO_x precursor formation due to primary and secondary pyrolysis.

Project Objective

At high heating rates ($> 10^4$K/s), primary coal pyrolysis begins at temperatures of 900 to 1000 K. Secondary pyrolysis is defined as the pyrolysis of volatile products that have already been released from the coal particles, and occurs at temperatures greater than 1100 K. At these higher temperatures, a small amount of additional nitrogen is also released as primary products from the char, generally in the form of HCN. Primary pyrolysis has been studied extensively, while less is known about secondary pyrolysis. Secondary pyrolysis can become more important in the fuel-rich regions created by air staging (both in low-NOx burners and in less localized staging concepts such as overfire air).

The goal of this project is to study the nitrogen transformations during secondary coal pyrolysis which occurs after primary devolatilization but before significant volatile combustion and char oxidation occur. The partitioning of nitrogen in the gas phase, char and soot will be measured. Special emphasis will be placed on the formation and evolution of NO_x precursors such as HCN and NH_3, and possibly HNCO. A model of secondary pyrolysis including tar reduction, soot formation, and nitrogen transformation will be developed in conjunction with the Chemical Percolation Devolatilization (CPD) model [1] to predict NO_x formation during pulverized coal pyrolysis.

Approach

Experiment

The major portion of the experimental work will be conducted in a flat-flame burner (FFB) operated in fuel-rich mode. This experiment provides a high temperature laminar flow reactor environment with no O_2 present in order to conduct secondary pyrolysis experiments. However, since minimum flame temperatures in the FFB are about 1600 K, several additional tests will be also made in a drop-tube reactor to provide data at lower temperatures.

Both CO and CH_4 can to be used as fuels in the FFB experiments. CO flames generate minimal H_2O, which is desirable since H_2O may greatly complicate the FTIR analysis in the gas phase. However, preliminary calculations using CHEMKIN-II showed that nitrogen precursors are sustained better in the post flame of a CH_4 flame. Therefore, both fuels will be examined.

Test variables

Influencing factors affecting soot formation and nitrogen release during secondary coal pyrolysis include temperature, residence time, coal rank, particle size, oxygen concentration and even moisture content. In this project, the following factors are chosen as the test variables :

1. *temperature*
2. *residence time*
3. *coal rank*
4. *CH_4 flame vs. CO flame*

The effects of the test variables on nitrogen transformations will be studied through experiments.

Accomplishments

Initial experiments are being conducted on an Illinois #6 and a Utah bituminous coal. Other two coals, including a Wyodak subbituminous coal and a Knife River lignite will be used in subsequent pyrolysis experiments. The coals were pulverized and sieved to obtain the 45-75 μm fraction, and then dried at 105°C for two hours before injection into the flat-flame burner (FFB). The ultimate and proximate analyses of the two coals are shown in Table 1. Ultimate analysis was performed on a LECO 932 CHNS elemental analyzer using coal sample sizes of approximately 1.5 mg.

Table 1. Ultimate and Proximate Analysis of Coals Used

Coal	Proximate analysis (wt%,db)			Ultimate analysis (wt%,daf)				
	ash	volatile matter	fixed carbon	C	H	N	O[†]	S
Illinois #6	12.435	42.695	44.870	76.004	5.476	1.523	12.317	4.680
Utah	9.817	44.495	45.688	81.436	5.873	1.639	10.500	0.533

[†] O=100-(C+H+N+S)

Experiments were performed in two temperature conditions in CO flames as a function of residence time. The equivalence ratio was adjusted to be approximately 1.20 to create a fuel-rich environment in the post flame region. The two conditions and their corresponding temperature profiles in the FFB are shown in Table 2 and Figure 1, respectively. The temperatures were measured using a type-B thermocouple (OMEGA Engineering) and corrected for radiation loss.

Table 2. CO Flame Conditions

peak temperature	Air (slpm*)	CO (slpm)	H_2 (slpm)	Dilution N_2 (slpm)	Carrier N_2 (slpm)	Quench N_2 (slpm)	Equivalence ratio
1640 K (condition 1)	19.5	12	0.35	10.2	0.0365	60	1.2058
1743 K (condition 2)	24.5	15	0.4	8	0.0365	60	1.2019

* slpm: standard litter per minute

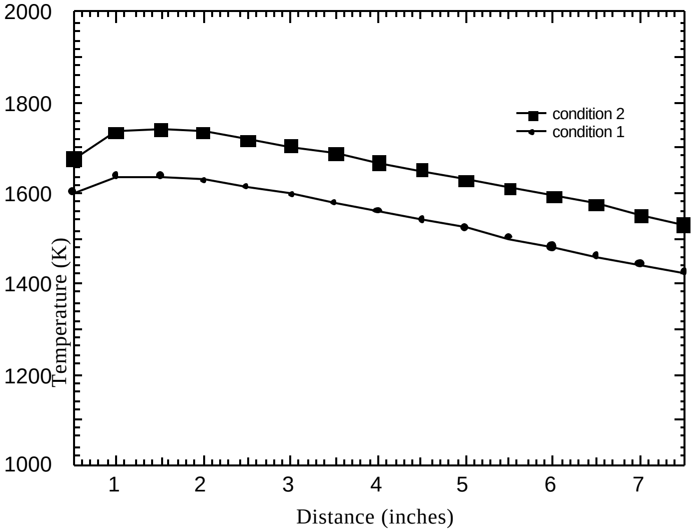

Figure 1. Centerline gas temperature profiles for CO flame conditions.

Mass release of coal was determined using an Inductively Coupled Plasma (ICP) method to determine mineral tracers, since measurement from directly weighing the mass of coal and char is not accurate. A nitrogen balance was performed from the elemental analyses of the char and soot; gas phase elemental composition in these figues is inferred by difference. The nitrogen distributions for the Illinois and Utah pyrolysis experiments in 1640 K CO flame are presented in Figures 1 and 2, respectively. The nitrogen distributions for the Illinois and Utah pyrolysis experiments in 1640 K CO flame are presented in Figures 2 and 3, respectively. These data show that the nitrogen in the soot initially increases with residence time for both coals, although the soot nitrogen begins to drop at long residence times for the Utah coal. The nitrogen in the gas phase demonstrates the same trend: an initial decrease of nitrogen in the gas followed by a steady increase. Nitrogen retained in the char decreases monotonically for the

Utah coal; while for Illinois coal, char nitrogen increases at early residence times but drops at longer residence times. Figures 4 and 5 show the nitrogen distribution in 1743 K CO flame. At higher temperature, the nitrogen distribution exhibited a different pattern. Nitrogen in the gas phase increases steadily, with a corresponding decrease in char-N. The fraction of nitrogen trapped in soot stays constant with increasing residence time. Considering the fact that the soot yield increases with residence time, it is obvious that the nitrogen content in soot decreases at higher residence time. During secondary pyrolysis, when tar and light gas undergo reactions leading to soot formation, char would release HCN and other nitrogen containing gases at the same time, resulting a continuous loss of nitrogen from char. [2]

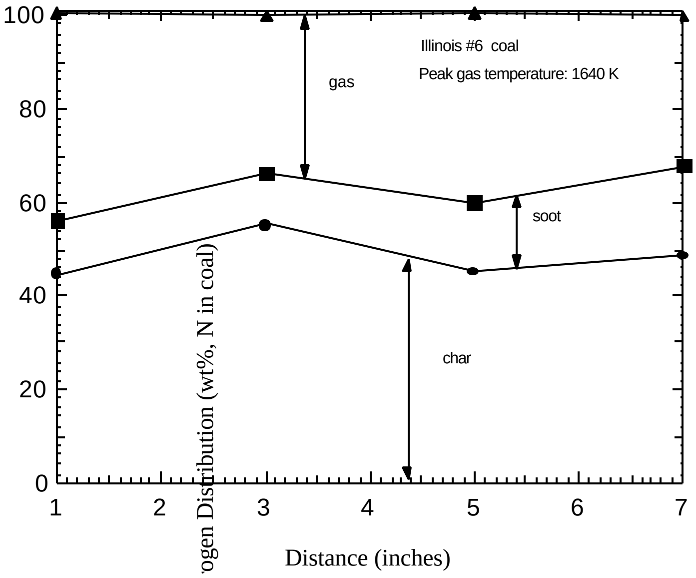

Figure 2. Cumulative nitrogen distribution for the Illinois #6 coal pyrolysis experiments in the 1640 K CO flame (condition 1).

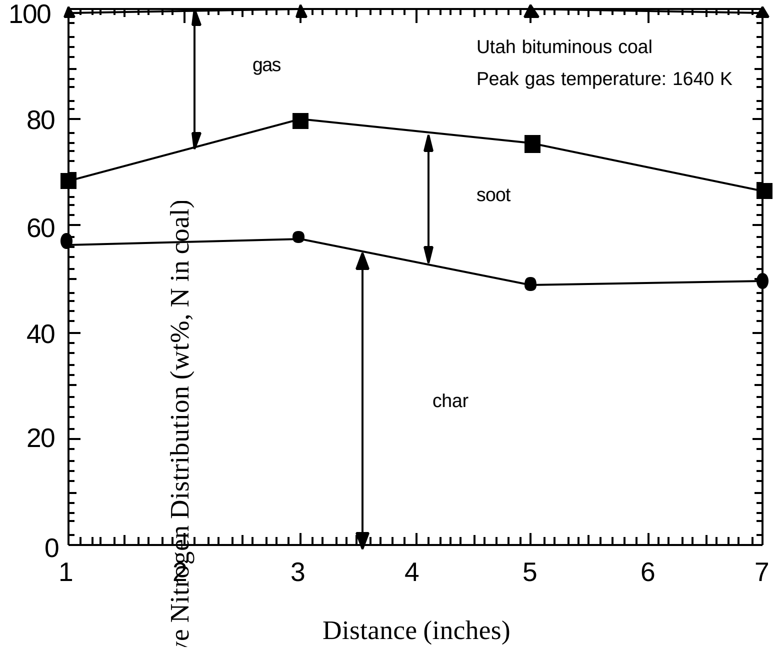

Figure 3. Cumulative nitrogen distribution for the Utah coal pyrolysis experiments in the 1640 K CO flame (condition 1).

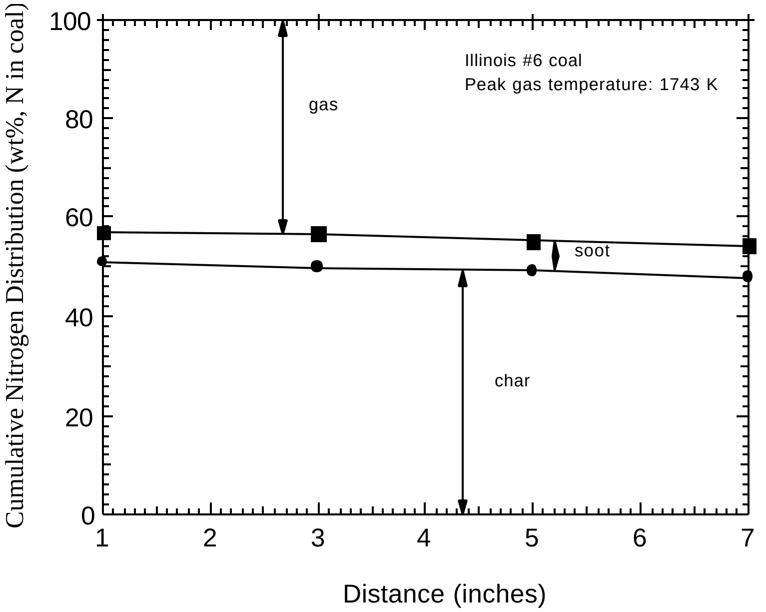

Figure 4. Cumulative nitrogen distribution for the Illinois coal pyrolysis experiments in the 1743 K CO flame (condition 2).

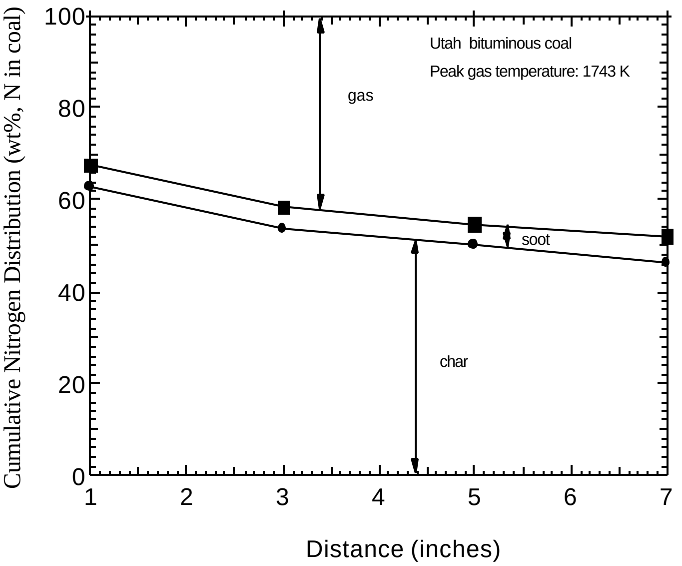

Figure 5. Cumulative nitrogen distribution for the Utah coal pyrolysis experiments in the 1743 K CO flame (condition 2).

The nitrogen/hydrogen molar ratio in the char, soot and gas for the two coals under two different conditions is presented in Figures 6 and 7. It is clear that most of the hydrogen in the coal was released at the beginning of pyrolysis (at least 60% of hydrogen release), which matches Solomon's results. [3] Hydrogen in char then decreases monotonically, which may relate to the release of HCN from char at higher temperatures. Hydrogen is released from the char faster than nitrogen, as shown in Figures 6-7. N/H ratios for char and soot are totally different for the two coals under same conditions showing clear rank dependence.

A dedicated HCN/NH_3 monitor (Zellweger Analytics, model 7100) was used at first in an attempt to measure HCN/NH_3 concentrations in the coal combustion flame. Data from preliminary tests were not reliable due to huge fluctuations, therefore, a BOMEM MB-155 FTIR was used to measure HCN, NH_3 and other important species (such as CH_4, C_2H_4, C_2H_2 etc.). FTIR presents a great advantage over other analytical methods. It is fast and has a very low detection limit. With a proper multi-path gas cell, detection at ~10 ppb levels is easy to accomplish. A single spectra can give quantitative analysis of all the species presented in the spectra. Usually several dedicated instruments are needed in order to measure the important species in combustion system. CO/CO_2 measurement needs non-dispersive IR; NO_x detection needs chemiluminience; hydrocarbons need high quality GC. FTIR presentes a solution to use one instrument to fit all the analysis needs. Quantitative analysis of all the species can be easily made using respective reference spectra. However, the large amounts of CO_2 and H_2O (ranging from several percent to 30%) which are inevitable products from combustion processes cause serious interference when measuring other trace species. Therefore, care must be taken to choose the proper frequency where the interested species absorbs. In addition, accurate and reliable reference spectra are needed in order to carry out a satisfactory subtraction.

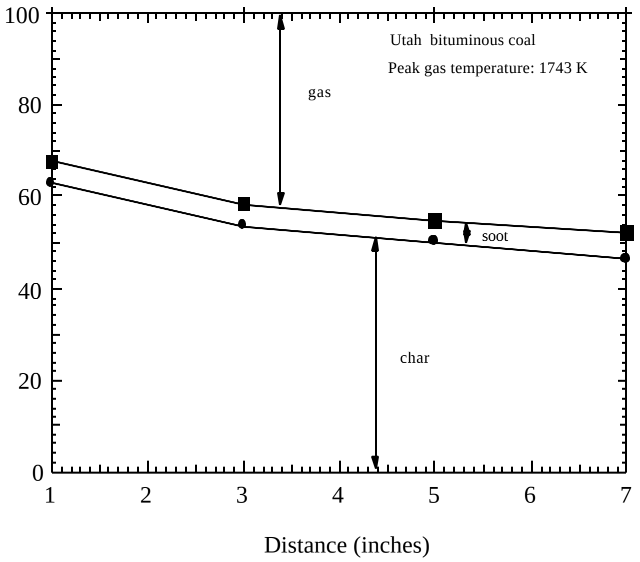

Figure 5. Cumulative hydrogen distribution for the Utah coal pyrolysis experiments

in the 1743 K CO flame (condition 2).

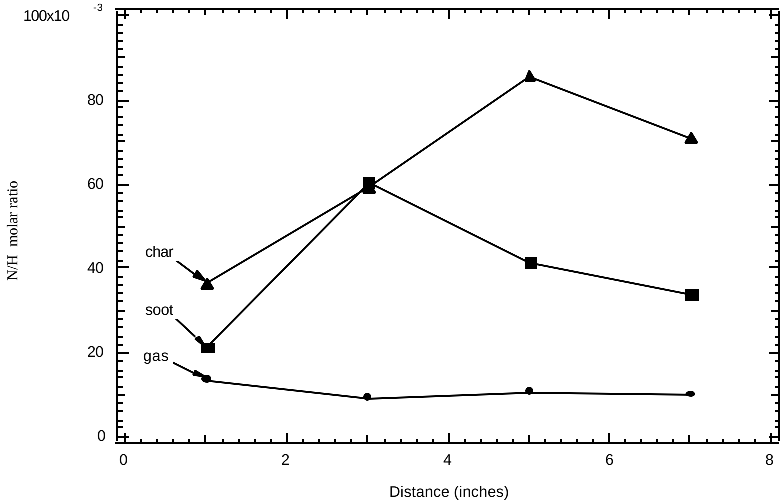

Figure 6. N/H ratios in the char, soot, and gas phase for the Illinois coal pyrolysis experiments in the 1640 K CO flame (condition 1).

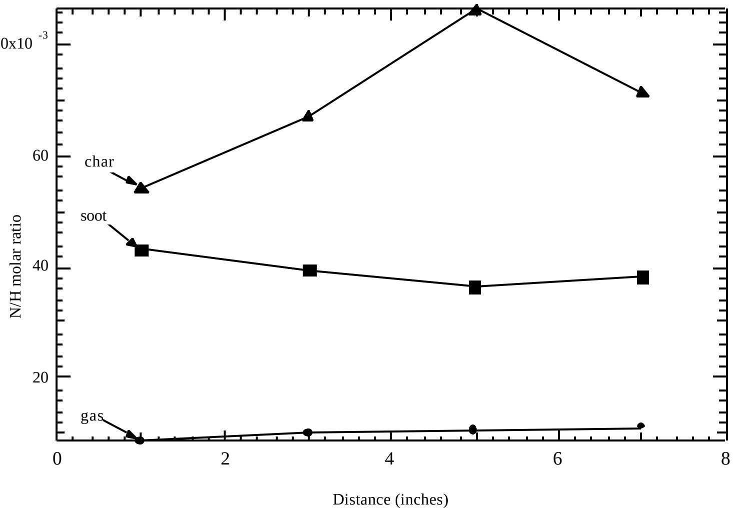

Figure 7. N/H ratios in the char, soot, and gas phase for the Utah coal pyrolysis experiments in the 1743 K CO flame (condition 2).

Future Work

Plans include testing additional coals with a wider range of rank from lignite to lvb bituminous. Two additional higher temperature conditions will be also tested for all the coals. Some supplementary experiments in the drop tube reactor will provide additional data for model development. A HP 6890 gas chromatograph will be used to detect the concentrations of hydrocarbons, CO, CO_2 and N_2 in the combustion gas.

References

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2. Nelson, Peter F., Buckley, Alan N., and Kelly, Martin D., 24th Symposium (International) on Combustion, The Combustion Institute, pp. 1259-1267 (1992).
3. Solomon, P. R., Serio, M. A., Suuberg, E. M., Coal Pyrolysis: Experiments, Kinetic Rates and Mechanisms, *Progress in Energy and Combustion Science*, 18, pp. 133-220, (1992).

Char Nitrogen Studies: Preliminary results on the study of char-N conversion to NO at pulverized combustion conditions

A review of the current literature on NO-char kinetics has shown that the governing chemical reactions are incompletely understood and that disagreement exists between the results of different researchers. Newly emerging quantum mechanical tools show promise of resolving some of these issues in the future.

However, in the interim and looking for an engineering approximation that may help on solving the problem of modeling the heterogeneous formation of NO from coal-N a simple model with a simple single NO formation step during char nitrogen oxidation and a first order reaction between NO and char has been used to generate a single particle model that captures the main characteristics of the NO-char kinetic reactions at pulverized combustion conditions. The model was calibrated with experimental data obtained during char combustion at pulverized coal conditions in a controlled atmosphere in a pilot scale combustor.

This report first summarizes the current knowledge on the kinetics of NO production at pulverized combustion conditions and then describes how the single particle model is incorporated to a CFD code in order to provide interesting insight of the role of char nitrogen on NO formation in pulverized coal boilers.

INTRODUCTION

NO_x from coal-fired boilers may be produced by a homogeneous or by a heterogeneous path, depending on whether the NO_x is formed from the nitrogen in the coal volatiles or in the residual char. Traditionally the nitrogen released during devolatilization has received more attention than that released during char oxidation, since it was reported to be the major contributor to NO_x and to be more amenable to control by modification of combustion zone aerodynamics and by air staging.[1] But as the NO_x from volatiles is controlled through the adoption of low-NO_x burners and staged combustion, the role of char in controlling the overall NO_x emissions has to be examined in greater detail.

The production of NO_x during char combustion and the kinetics of the nitric oxide-carbon reaction have recently being thoroughly reviewed by Thomas[2] and Aarna and Suuberg[3] respectively. Thomas[2] presented with great detail all the process of NO_x production. He described the structural changes of the N containing functionalities in the coal to char nitrogen functionalities and the proposed mechanisms for the NO reduction on the char surface and for the char-N conversion to NO and N_2O during pulverized and fluidized bed combustion. Aarna and Suuberg[3] reviewed the nitric oxide - carbon reaction in relation to the rates of the process, as opposed to detailed consideration of mechanism. Their review encompassed more than fifty different rate expressions for the NO-carbon reaction. They also analyzed the influence of coal rank, catalytic matter, heat treatment, mass transfer and other gases (CO, H_2O, CO_2 and O_2) concentration on the reaction rate.

A review of the literature underlines the great uncertainty on both mechanisms and rates of char nitrogen oxidation to NO and the rate of NO reduction by char. However, the use of an approximate model may capture some of the major features of the chemistry but simple enough to fit available laboratory data on the NO-char reactions adequately for use in CFD calculations. This model may be further used to perform representative calculations of the role of char particles on the net rate of NO emissions allowing for both the formation of NO from char nitrogen and the destruction of NO by the char-NO reactions.

N CONTAINING FUNCTIONALITIES IN COAL AND CHAR.

The first step is to identify the nitrogen functionalities present in coal and in char. These consist[2] basically of pyrrolic (50 - 80%), pyridinic (20 - 40%) and quaternary nitrogen (0 - 20%). Small amounts (<10%) of amino groups may be present in low rank coals.

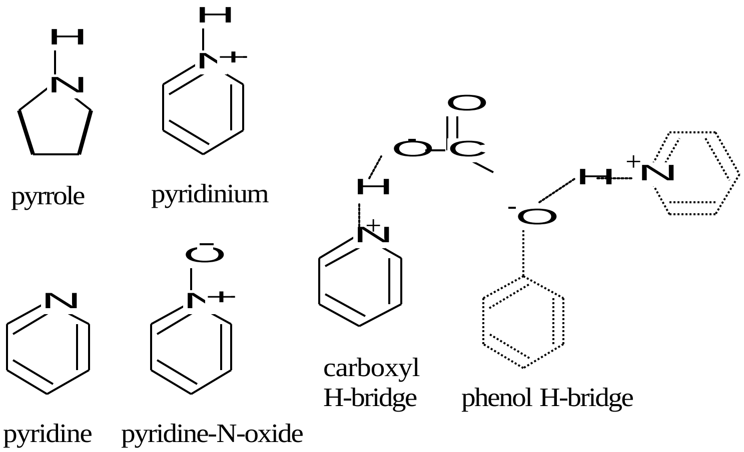

Figure 1. Most possible nitrogen functionalities present in coal. [4-7]

The groups rearrange during pyrolysis and at higher temperatures the formation of quaternary nitrogen in graphene layers, as shown in Figure **2**, has been postulated.[4]

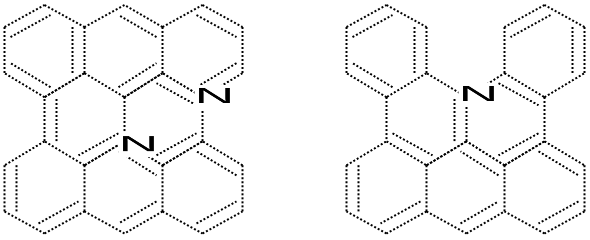

Figure 2. Suggested structure of quaternary nitrogen after pyrolysis.[4]

After mild pyrolysis (T < 650°C) there is an increase of pyridine groups, as the concentration of pyrrole and quaternary nitrogen is reduced.

The effect of the nitrogen functionalities on the rate of NO formation is believed to be small[4,7] although this is not universally accepted.[8] The view in this paper is that the functional form of nitrogen has a secondary effect compared to those of other parameters such as catalysts, char surface area, and pore size distribution.

MECHANISMS OF NO PRODUCTION DURING CHAR OXIDATION.

The mechanisms that govern the NO production during oxidation are those involving the release of the char bound nitrogen, its subsequent oxidation to NO, and the reduction of NO by char, including NO produced by other particles, volatile nitrogen and thermal NO_x. The NO formation and destruction reactions are closely coupled to the char oxidation reactions and are best considered together. The comprehensive phenomenological model of de Soete[9] can be used to understand the more important classes of reaction:

$$O_2 + 2(-C) \rightarrow C(-CO) \qquad \text{R 1}$$

$$(-CO) \rightarrow CO + \text{free carbon site} \qquad \text{R 2}$$

$$2(-CO) \rightarrow CO_2 + \text{free carbon site} \qquad \text{R 3}$$

$$O_2 + (-C) + (-CN) \rightarrow (-CO) + (-CNO) \qquad \text{R 4}$$

$$(-CNO) \rightarrow NO + (-C) \qquad \text{R 5}$$

$$NO + (-C) \rightarrow (1/2)N_2 + (-CO) \qquad \text{R 6}$$

$$NO + (-CNO) \rightarrow N_2O + (-CO) \qquad \text{R 7}$$

By a series of carefully designed transient experiments he has been able to obtain the rate constants for these reactions. The reactions can be used to fit the data on NO formation from char nitrogen and also the reduction of NO by char and to show the importance of different pathways.[9]

However, it is difficult to fit all observations with a simple set of reactions. The rate of reaction leading to NO and N_2O are found to be accelerated by the presence of O_2 which is believed to help open the aromatic nitrogen containing rings. HCN has been observed in coal char oxidation, particularly of those with high hydrogen content or in the presence of water vapor.[10] Use of iodine to quench free radicals in the gas phase has changed the product distribution significantly suggesting that the char nitrogen may be released as HCN.[11] The measurement of the gas phase species close to the surface and the examination of the effect of isotopic nitrogen tracers provide more details on the reactions which cannot be explained by phenomenological models. At low temperatures char nitrogen complex may be formed from the reaction of NO with char.[10,12,13]

MECHANISTIC MODELS

The mechanism of the char nitrogen reactions will probably be resolved using mechanistic studies similar to the recent molecular orbital calculations[14-17] that have been used to develop reaction pathways for the oxygen/carbon reactions.

According to *Ab Initio* molecular orbital calculations of Chen and Yang,[14] the C-O_2 reaction proceeds as shown in Figure 3.

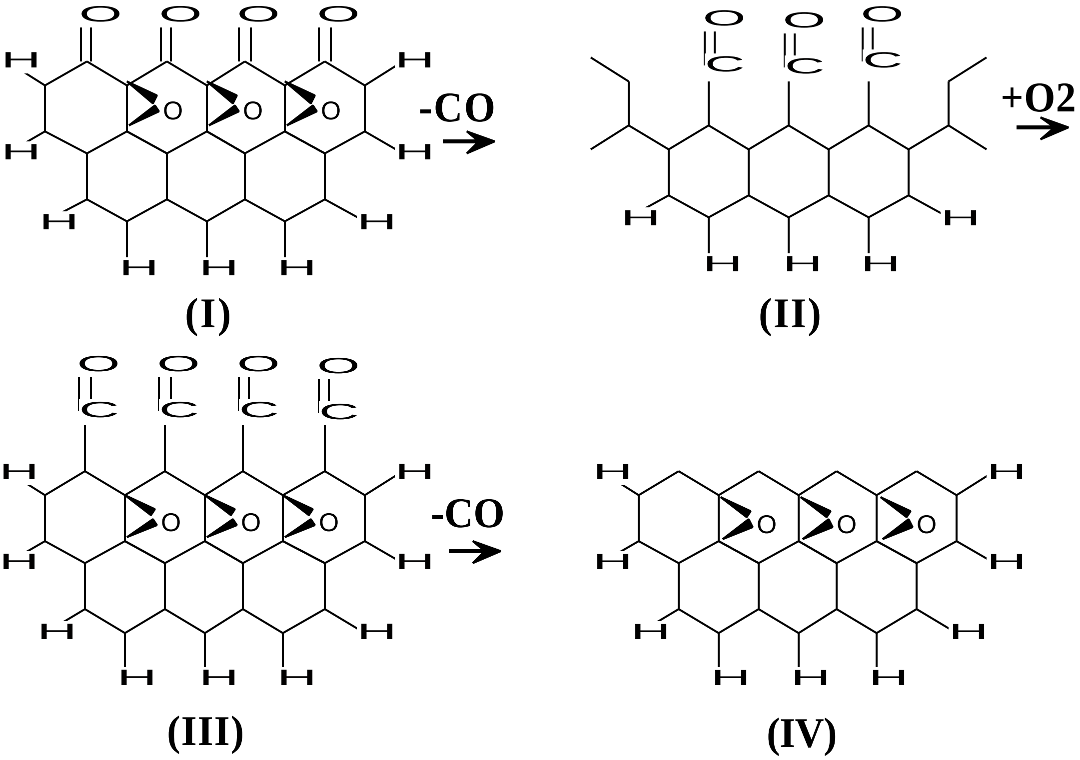

Figure 3 Reaction pathway for the graphite - O_2 reaction.[14]

Chen and Yang[14] showed that the "epoxy" oxygen, this is the one out of the plane, or on the basal plane, reduces the strength of the C-CO bond, and CO is released from the molecule (Structure I). The epoxy oxygen flips over to the edge, and transforms in a new carbonyl structure (II). New oxygen chemisorption will produce structure (III), the carbonyl groups break and oxygen chemisorption will occur, this time in the edge plane, to transform structure IV back to structure I.

The issues involved in the use of molecular orbital methods include the level of theory used[4,14,15,17-21] and the approximation of solids such as graphite, by finite structures, as in Figure 3. Chen and Yang[18] addressed both issues, the level of theory required, and the size and nature of the graphite cluster used for modeling the system. A structure similar to Figure 3 ($C_{25}H_9$) and the calculation level B3LYP/6-31G(d) were their recommendations. Despite this theoretical analysis, further experimental support and extended molecular orbital calculations are needed in order to confirm the validity of mechanisms such as those discussed above.

By analogy to the structures proposed for the oxygen/carbon reactions, Figure 4 presents a possible structure for nitrogen-containing char during oxidation. This figure attempts to bring together the previous description of chemisorbed oxygen, both in the edge and basal plane, and the existence of pyridinic (N7 and N8) and quaternary nitrogen (N9).

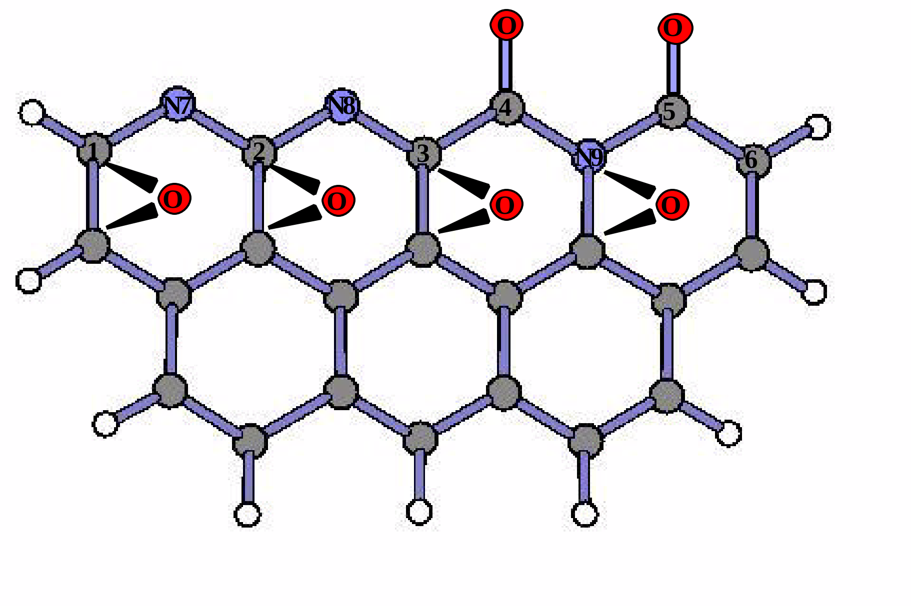

Figure 4. Possible structure of graphite before nitrogen evolution.

By an analogy with the mechanism proposed by Chen and Yang[14] for char oxidation (Figure 3), we may expect some of the following compounds to be formed from a structure as in Figure 4.

- **HCN**: The epoxy adsorbed oxygen will weaken the C2 - N7 bond, and an HCN molecule may be released. This HCN will react in the gaseous phase to produce NO.

- **CN:** As in HCN production, the epoxy oxygen will weaken the C2 - N8 bond and CN may be formed. Further homogeneous reactions (R 8 to R 11) will convert CN to NCO that is then converted to NO.

$$CN + OH \leftrightarrow NCO + H \qquad \text{R 8}$$
$$CN + O \leftrightarrow CO + N \qquad \text{R 9}$$
$$CN + NO_2 \leftrightarrow NCO + NO \qquad \text{R 10}$$
$$CN + N_2O \leftrightarrow NCO + N_2 \qquad \text{R 11}$$

- **NO** and **CO**: By a process similar to that described in Figure 3, CO will be released from C4 and C5 and their associated semiquinone oxygens. The epoxy oxygen then flips over to the edge side and a NO molecule is formed at N9.

The possibility of the occurrence of these reactions may be determined by molecular orbital calculations, coupled to analysis of experimental results.

SINGLE PARTICLE MODEL FOR PREDICTION OF NOX FORMATION FROM CHAR-N.

From the previous discussion it is clear that there are uncertainties in the phenomenological description of the char-NO_x reaction, both for NO production from char, and for its reduction on char surface. However, in order to obtain engineering solutions, some approximations are justifiable.

For char-NO_x kinetics, the following four approximations have proven to be useful for developing a mathematical model for the reaction.

1. *Nitrogen evolution during char oxidation is assumed to be proportional to carbon consumption. The ratio between nitrogen and char atoms is the proportionality constant*.

Baxter et al[1] have shown that this is not true for different chars. Nevertheless, several authors[22-24] have found this approximation valid for different chars.

2. *NO is the main product of char-N oxidation.* As stated above, there is no unambiguous evidence of the direct heterogeneous formation of NO. The presence of HCN as intermediate is considered possible. However, as an approximation, it is reasonable to assume that NO is the main product at pulverized coal combustion conditions, and that any HCN produced is rapidly oxidized to NO.

3. *The reduction of NO on char surface is important and may be considered to be a first order reaction.* Thomas and coworkers[25-28] showed that more reactive chars tend to have less char-N to NO conversion when submitted to temperature programmed oxidation. They attributed this fact to the lower NO reduction capacity of less reactive chars. This underscores the importance of NO reduction on char surface during char oxidation.

Regarding the reaction order, Aarna and Suuberg,[3] showed that most of the literature on the kinetics of the NO-carbon reaction considers this to be first order with respect to NO, although some exceptions are found.[29] Aarna and Suuberg postulated[3,30] that this may be explained by the influence of CO on this reaction. Therefore, the selection of first order for this reaction is not only supported by experimental data, but it also simplifies reaction modeling as will be seen.

4. *The influence of oxygen on the reduction of NO on char surface may be neglected.* Recent work by Linares-Solano and coworkers,[31] Ciambelli et al[32] and Lizzio et al[33] stressed the importance of oxygen in the reduction of NO on char surface, when carbonaceous materials loaded with catalyst were considered and at relatively low temperatures (<900 K). Tomita and coworkers,[13] have also studied the influence of O_2 on the NO - char reaction, and at

temperatures closer to pulverized coal combustion (1123 K). They also found that O_2 favored this reaction, and suggested the activation of $C(N)$ species as the most possible explanation of this fact. Despite this, the effect of O_2 on the NO-char reaction may as a first approximation be neglected. One justification[34] for this approximation is that the oxygen-char reaction is two orders of magnitude faster than the NO-char reaction. Therefore, during combustion, O_2 will be rapidly consumed, and its concentration inside char's micro-pores (where NO reduction takes place) may be negligible.

These approximations were used to implement a single particle model, similar to that described by Wendt and Schulze[35] and more recently by Visona and Stanmore[36] and Goel et al,[37] for the prediction of char-N conversion to NO.

The main assumptions of the model are:

- A spherical char particle, pseudo-steady state and constant effective diffusivity.
- Reactions considered: carbon oxidation: $-C+\frac{1}{2}O_2 \xrightarrow{k_{O_2}} CO$, NO formation: $O_2+-CN \xrightarrow{k_0} NO$ and NO reduction: $NO+-C \xrightarrow{k_{NO-C}} N_2+-C(O)$.
- The rate expression for the reaction O_2-carbon is from Smith.[38] NO production is proportional to the nitrogen/carbon atomic ratio of the char. The rate expression for NO reduction is first order with respect to NO: $R^v_{NO}=\frac{1}{0.5}\left(\frac{N}{C}\right)k_{O_2}C_{O_2}-k_{NO}C_{NO}$.

Since all rate expressions are first order with respect to all reactive species, an analytical solution of the species mass conservation equation can be derived. This allows predicting the conversion of char-N to NO for any char particle, for a given coefficient for the reaction rate of

NO reduction on char surface (k_{NO}) and for specified physical parameters such as effective diffusivity, particle surface area, char porosity, and particle density.

In order to test the model, data[39] of the formation and reduction of NO during char combustion at pulverized coal conditions were used. Spinti's[39] experiments were performed in the 29 kW U furnace of the University of Utah, the description of which is presented elsewhere.[39,40] One of the objectives of that study was to obtain all data at pulverized coal combustion conditions. This was done by collecting particles near the burner, while burning coal. The collected chars were afterwards combusted in the same furnace, where simultaneous natural gas oxidation simulated volatiles combustion. Ammonia was added to the burner to simulate different levels of NO production. Figure 5 presents some of Spinti's results. In these experiments, the initial concentration of NO_x was increased, and the conversion of char-N to NO_x was measured for four different coals. It is clear that as NO_x concentration is increased, the amount of char-N conversion to NO_x is reduced for all the chars tested. This may be understood as an increase of NO_x reduction during the process. It also indicates that NO_x reduction on the char surface should not be neglected during pulverized coal combustion.

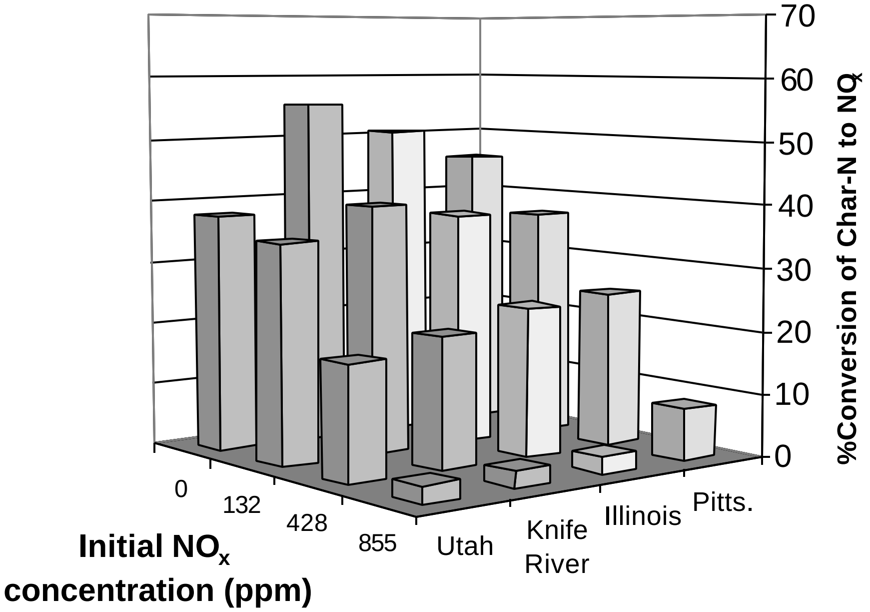

Figure 5. Influence of initial NO$_x$ concentration on char-N conversion to NO$_x$. Data from Spinti.[39]

The model was fitted to the data of Spinti[39] by using a least square method to determine $k_{NO.}$ Figure 6 presents a comparison between model predictions and experimental data. k_{NO} was the only parameter varied; all other parameters were found from Spinti's[39] experimental data or assumed to be similar to those reported in the literature.[36] Results for chars of different coals were similar to those of Figure 6.

Although the agreement is best for low NO$_x$ bulk concentration, the results are encouraging, especially when considering the assumptions made in using a single particle model to approximate char combustion in a self-sustained flame.

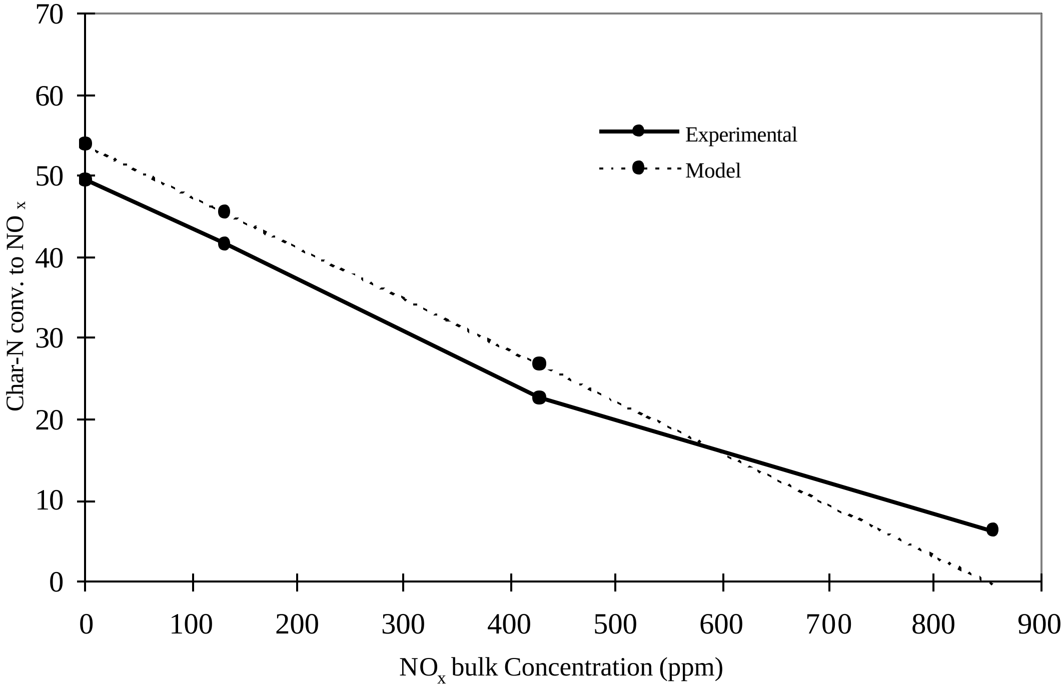

Figure 6. Comparison between experimental and model predictions of char-N conversion to NO_x as NO_x bulk concentration is increased. Illinois #6,

IMPLICATIONS TO THE NO EMISSIONS IN BOILERS.

With a model of char nitrogen conversion in hand, the influence of char-N on NO formation in a pulverized coal combustor was applied as a post-processor for the prediction of NO formation from coal particle trajectories, as predicted by GLACIER. GLACIER is a reacting computational fluid dynamic (CFD) code designed for modeling three-dimensional reacting two-phase flows using a Lagrangian particle plume tracking technique.[41] The information obtained from GLACIER included particle temperature and diameter, char concentration in the particle, and NO and O_2 concentration outside the particle for each time step.

With these input data, the single particle model allowed the prediction of the cumulative conversion of char-N to NO (F_{NO}). F_{NO} was defined as the ratio between the cumulative moles of NO produced or reduced during particle trajectory and the total number of moles of NO that would be formed if all char-N originally in the char was converted to NO, $F_{NO} = \frac{\int_0^{t_f} \left(-4pR_p{}^2 D_e \left.\frac{dC_{NO}}{dr}\right|_{r=R_p} \right) dt}{\frac{4}{3} p \left(\left. R_p \right|_{t=o} \right)^3 r(\%\ \mathrm{N\ inchar}) \frac{1}{Mw(N)} 1000} *100$ Where $\left.\frac{dC_{NO}}{dr}\right|_{r=R_p}$ was determined from the solution of the species mass transfer equation and other terms are as described in nomenclature. According to this definition a positive slope of the plot of F_{NO} vs time indicates that NO flows in the outward direction. That is, $\left.\frac{dC_{NO}}{dr}\right|_{r=R_p} < 0$. However, if NO production inside the particle is smaller than the NO consumption by the reduction reaction, $\left.\frac{dC_{NO}}{dr}\right|_{r=R_p} > 0$ and a negative slope, and eventually a negative value of F_{NO} are also possible. In this case the char particle will be reducing the NO present in the surrounding atmosphere.

A total of 3456 different particle trajectories were analyzed, for two different cases. Two examples of particle trajectories are presented in Figure 7 and Figure 8. These figures present the weight fraction of char in the coal particle (X_{char}), the oxygen and NO_x bulk concentration and the temperature vs. residence time as predicted from GLACIER. At the bottom of each figure, the value of F_{NO} as computed by the single particle model is also presented. Figure 7 presents an average trajectory. F_{NO} increases from 0 to ~15% during char oxidation. Once the char is oxidized, there is no additional change in F_{NO}. Figure 8 presents an extreme case, where reduction occurs (negative F_{NO} value). For this particle, the low oxygen concentration promotes a reducing atmosphere, therefore NO is destroyed. Figure 9 presents the percent of particles with conversion less than a given value of F_{NO} for the two boilers analyzed. One case was for a boiler without NO_x control strategy (Pre-Low NO_x) and in the other case, a NO_x control strategy (low NO_x burner with overfire air) was implemented. For both cases, more than 30% of the particles are actually reducing NO, while at the opposite extreme there are particles with F_{NO} values as high as 90%.

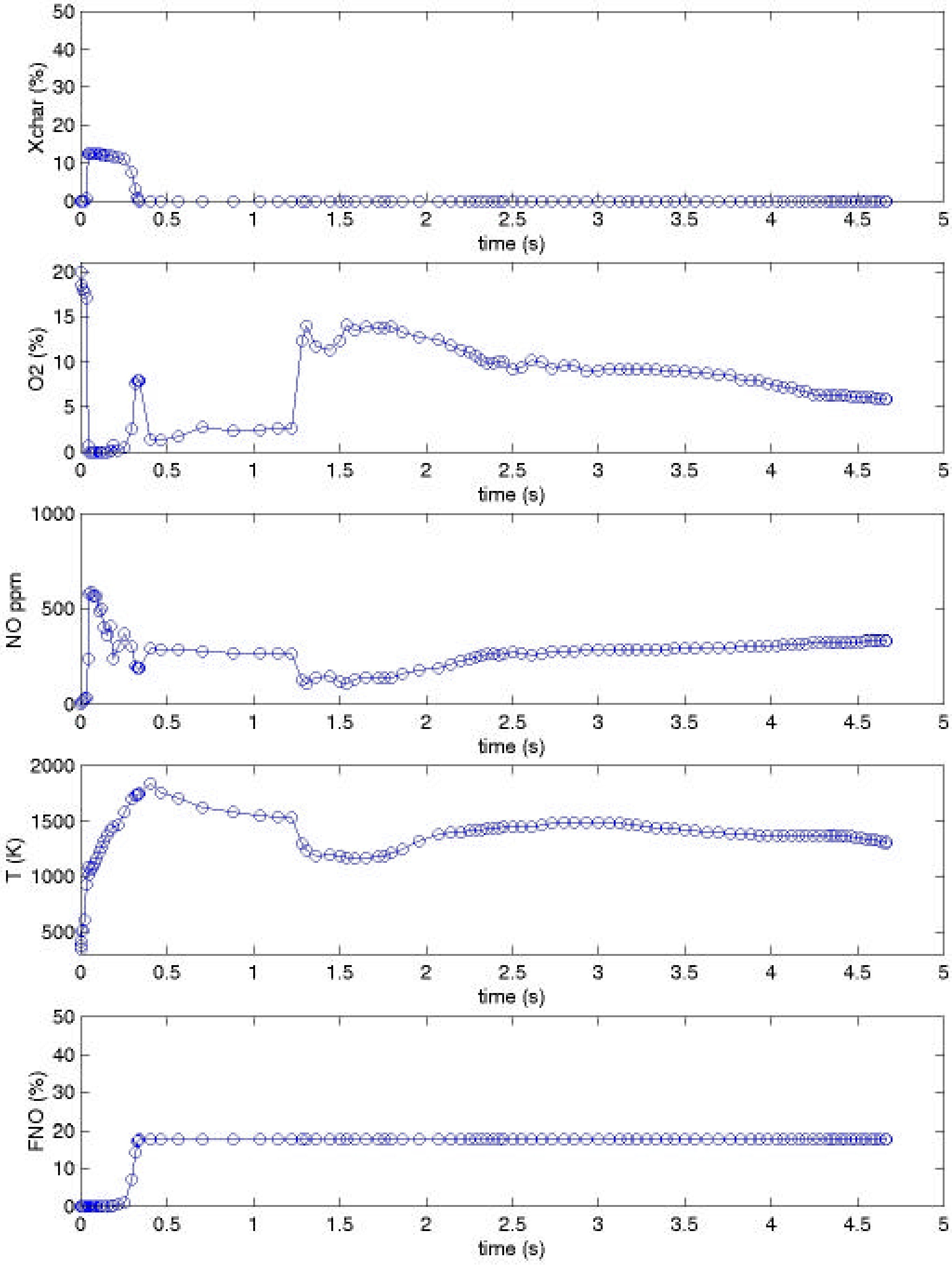
Xchar (%)
0
10
20
30
40
50
O2 (%)
0
5
10
15
20
NO ppm
0
500
1000
T (K)
500
1000
1500
2000
FNO (%)
0
10
20
30
40
50
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
time (s)

Figure 7. Char conversion, Oxygen and NO bulk concentration, particle temperature, and char-N conversion to NO as predicted by Glacier and single particle model. Particle submitted to oxidizing atmosphere

Average values of char-N conversion to NO_x were computed from Figure 9 and are in Table 1. Average values of O_2 and NO concentration are also shown for the time when char particles were present. The values of F_{NO} are between the range reported by Pershing and Wendt[42] for similar pulverized coal combustion conditions.

The increase of F_{NO} for the Post-Low NO_x case seems to contradict the results of Figure 5, where higher NO_x concentration implied lower char-N conversion to NO. However in the experiments leading to the results in Figure 5, the O_2 concentration was the same for all NO_x concentrations. In contrast, the figures of Table 1 show that the Post-Low NOx case presents lower O_2 concentration, and we may expect the effect of higher NO concentration be compensated by that of high O_2 concentration.

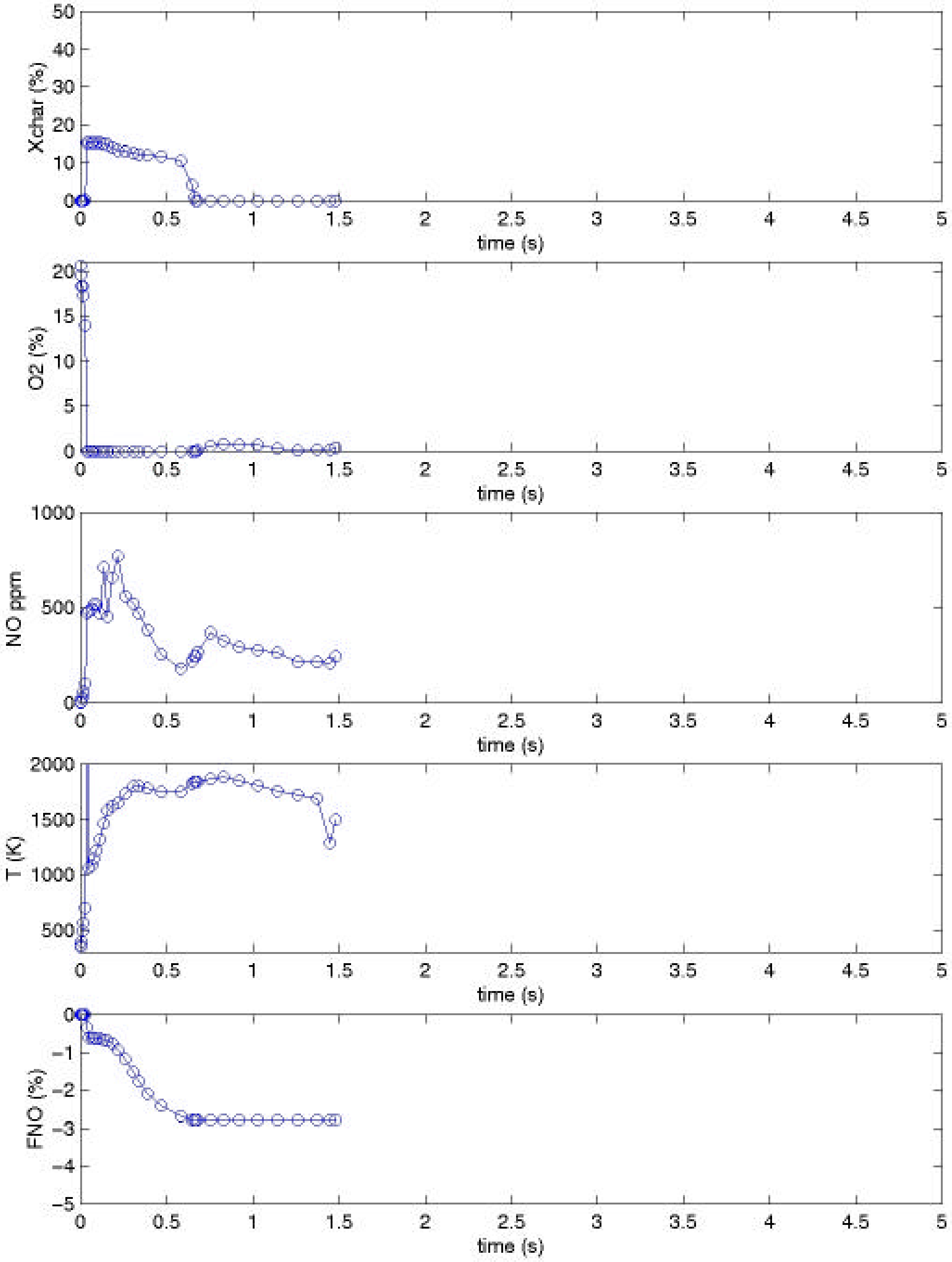
Xchar (%)
50
40
30
20
10
0
O2 (%)
20
15
10
5
0
NO ppm
1000
500
0
T (K)
2000
1500
1000
500
FNO (%)
0
−1
−2
−3
−4
−5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
time (s)

Figure 8. Char conversion, Oxygen and NO bulk concentration, particle temperature, and char-N conversion to NO as predicted by Glacier and single particle model. Particle submitted to reducing atmosphere.

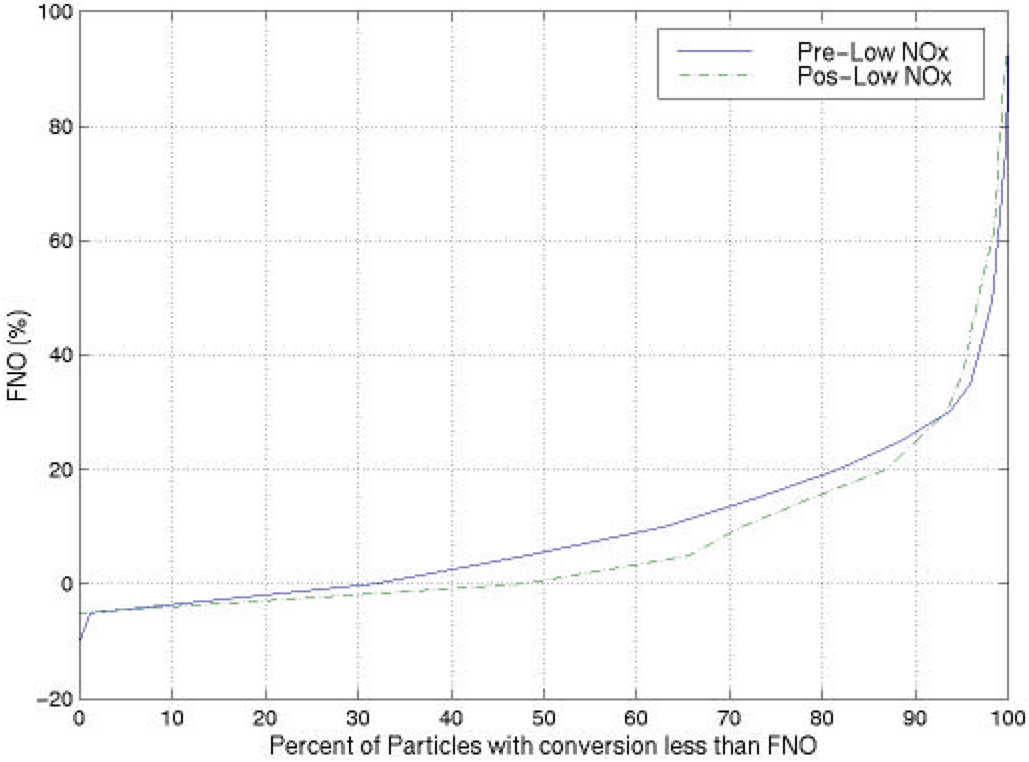

Figure 9. Distribution of char-N conversion to NO, F_{NO}, as predicted by the single particle model.

Table 1. Summary of the predictions from Glacier and from the single particle model for coal combustion at pulverized coal conditions.

Case	Pre-Low NO_x	Post-Low NO_x	Pre/Post
Number of trajectories	1920	1536	-
F_{NO} (%)	11.7	9.7	-
NO_x average (ppm) when char is present	474	309	1.5
O2 average (%) only when char is present	5.9	3.0	2.0

The above information shows that char particles play an important role, both in NO formation and destruction, and the magnitude of this role depends on char properties and the environment surrounding the char particle. The mechanistic model helps determine the effects of competing phenomena such as those of the changing O_2 and NO during air staging. Further refinements of the model are needed as uncertainties in the mechanisms and rates are resolved.

NOMENCLATURE

Ap: Particle surface area, m^2 kg-1
Concentration of species i, mol m-3
Effective diffusivity, m^2 s-1
F_{NO}: Cumulative conversion of char-N to NO
Mw: Molecular weight, kg mol-1
Rp: Radius of the particle, m
Radial position, m
t: Time, s
r : Particle density, kg m-3

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