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 NO_x 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 NO_x 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, and reporting will be divided into these main areas:

- 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 University 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 continues 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 ($> 10^4 \text{K/s}$), 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- NO_x 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 . 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

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.

Accomplishments

A literature review of previous secondary coal pyrolysis experiments was performed to gather published data on elemental compositions of tar, char, and soot under various conditions. A review of pertinent gas analysis techniques was also performed to identify appropriate methods to measure gas species such as HCN, NH_3 , HNC, and NO under the highly diluted conditions of the flat flame burner (FFB) experiment. Mass flow controllers were obtained for the FFB to better control the stoichiometry and gas velocity. Normal operation of the FFB uses CH_4 and H_2 as the fuel, and air and N_2 mixed together to provide the oxidizer stream. The resulting post-flame conditions (i.e., gas temperature and gas species concentrations) are ideal for secondary pyrolysis, but the high steam concentrations (18 mole-%) inhibit the use of spectroscopic techniques for measuring HCN and NH_3 concentrations. Therefore, a CO flame was investigated as a means to reduce the amount of steam produced from natural gas-fired experiments. A small amount of H_2 must be added to the CO flame to stabilize the flame, but initial results seem quite promising. Finally, two coals were obtained from the University of Utah for preliminary pyrolysis experiments.

Future Work

Plans for the next reporting period include initial coal pyrolysis tests in the FFB using a CO flame. Char and tar samples will be collected and analyzed for nitrogen content.

References

1. Fletcher, T. H., A. R. Kerstein, R. J. Pugmire, M. S. Solum, and D. M. Grant, "A Chemical Model of Coal Devolatilization: 3. Direct Use of ^{13}C NMR Data to Predict Effects of Coal Type," *Energy and Fuels*, **6**(4), 414-431 (1992).

Char Nitrogen Studies: Single Particle Model for NO_x Formation During Pulverized Coal Combustion

In order to obtain a better understanding of the process of NO_x production at PC conditions, a single particle model for the heterogeneous formation of NO_x during coal combustion is developed. This model is a simplification of a previous study by Goel and Sarofim.¹

1. Governing Equation.

Assuming the char particle as a sphere and considering pseudo-steady state and constant effective diffusivity, the equation which represents the mass balance for each species i is:

$$\frac{-D_e}{r^2} \frac{d}{dr} \left(r^2 \left(\frac{dC_i}{dr} \right) \right) = R_i^v \quad (1)$$

where r : radial position (m), D_e : effective diffusivity (m² s⁻¹), C_i : concentration of species i (mol m⁻³) and R_i^v : volumetric reaction rate (mol m⁻³ s⁻¹)

With the following boundary conditions:

$$\text{At } r = 0, C_i \text{ is finite} \quad (2)$$

At $r = R_p$,

$$D_e \left. \frac{dC_i}{dr} \right|_{r=R_p} = k_g (C_i^b - C_i^s) \quad (3)$$

Where R_p : radius of the particle (m), k_g : mass transfer coefficient (m s⁻¹), C_i^b : concentration of species i in the bulk (mol m⁻³), C_i^s : concentration of species i at $r = R_p$ (mol m⁻³).

2. Reactions.

The model considers the following heterogeneous reactions:

- Carbon oxidation:

- NO formation:

- NO reduction:

This is a simplification of the real process. Here only the CO production by char oxidation was considered, neglecting the CO₂ contribution. NO is considered to be only reduced by the char surface, although it has been shown² that CO enhances NO reduction. And NO is considered as the exclusive product of char-N oxidation, neglecting the production of HCN or N₂O.

Since at high temperatures (as those of PC combustors) the carbon oxidation is more likely to produce CO than CO₂³ the first assumption is not expected to induce a high error. Also the N₂O production at PC conditions is very low compared to the NO yield.⁴ Therefore the assumption with higher influence in the results may be not considering CO and other species in the NO reduction.

The model leads to the following rate expressions:

$$R_{O_2}^v = -k_{O_2} C_{O_2} \quad (7)$$

$$R_{NO}^v = \frac{1}{\nu_{O_2}} \left(\frac{N}{C} \right) k_{O_2} C_{O_2} - k_{NO} C_{NO} \quad (8)$$

In the derivation of the rate expression for NO formation, it was assumed that the oxidation rate for nitrogen is equal to the oxidation rate of carbon times N/C. Where N/C is the nitrogen to carbon atomic ratio for the char. N/C is assumed constant through the process of char combustion. k_{O_2} is the coefficient for carbon oxidation reaction (s⁻¹), k_{NO} for NO reduction on the char surface and $\nu_{O_2} = 0.5$ is the stoichiometric coefficient for carbon-oxygen reaction.

3. Analytical Solution.

In this study, equation (1) is solved for O₂ and NO. The analytical solution, is next described.

3.1 Oxygen

For oxygen, $R_i^v = -kC_i$ and a solution to equation (1) is:⁵

$$C_{O_2} = \frac{c_1}{r} \sinh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) + \frac{c_2}{r} \cosh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) \quad (9)$$

By applying the boundary condition (2), equation (9) becomes:

$$C_{O_2} = \frac{c_1}{r} \sinh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) \quad (10)$$

Or in dimensionless form:

$$C_{O_2} = \frac{c_1}{R_p} \frac{\sinh(\phi_{O_2} \xi)}{\xi} \quad (11)$$

Where c_1 is a constant evaluated form the boundary condition (3):

$$\frac{c_1}{R_p} = \frac{ShC_{O_2}^b}{\sinh(\phi_{O_2})(Sh + \phi_{O_2} \coth \phi_{O_2} - 1)} \quad (12)$$

$\phi_{O_2} = \left(\frac{k_{O_2}}{D_e}\right)^{1/2} R_p$, $Sh = \left(\frac{k_g}{D_e}\right) R_p$ are modified Thiele and Sherwood numbers respectively,

and $\xi = r / R_p$ is the dimensionless radius.

3.2 NO

An analytical solution of equation (1) is:

$$C_{NO} = \left(\frac{1}{\xi(\phi_{O_2}^2 - \phi_{NO}^2)} \right) \left\{ -c_3 \sinh(\phi_{O_2} \xi) - B_1 (\phi_{NO}^2 \sinh(\phi_{NO} \xi) - \phi_{O_2}^2 \sinh(\phi_{NO} \xi)) \right\} \quad (13)$$

Where $c_3 = \frac{1}{v_{O_2}} \left(\frac{N}{C} \right) \left(\frac{c_1}{R_p} \right) \phi_{O_2}^2$ is a constant, B_1 and B_2 are integration constants and

$$\phi_{NO} = \left(\frac{k_{NO}}{D_e} \right)^{1/2} R_p \text{ is the modified Thiele modulus for NO.}$$

By applying the boundary conditions (2) and (3) equation (13) simplifies to:

$$C_{NO} = c_4 \frac{\sinh(\phi_{O_2} \xi)}{\xi} + c_5 \frac{\sinh(\phi_{NO} \xi)}{\xi} \quad (14)$$

With:

$$c_4 = \frac{c_3}{(\phi_{NO}^2 - \phi_{O_2}^2)} \quad (15)$$

$$c_5 = \frac{(\phi_{O_2}^2 - \phi_{NO}^2) C_{NO}^b Sh + c_3 [\phi_{O_2} \cosh(\phi_{O_2}) - \sinh(\phi_{O_2})] + c_3 Sh \sinh(\phi_{O_2})}{(\phi_{O_2}^2 - \phi_{NO}^2) \{ Sh \sinh(\phi_{NO}) + [\phi_{NO} \cosh(\phi_{NO}) - \sinh(\phi_{NO})] \}} \quad (16)$$

4. Mass transfer and kinetic parameters.

In order to determine the NO and O₂ concentration profiles it is necessary to find the kinetics and mass transfer parameters used by the analytical solutions stated above. To compare this analytical solution with Visona and Stanmore's study,⁶ the same parameters as those of these authors were used.

4.1 Mass transfer parameters.⁶

Effective diffusivity D_e (m² s⁻¹):

$$\frac{1}{D_e} = \frac{1}{D_{knud}} + \frac{1}{D_{bulk}} \quad (17)$$

Where $D_{knud} = \frac{24.25\epsilon^2 T^{0.5}}{A_p \rho_p}$ is de Knudsen diffusivity and $D_{bulk} = 1.28 \times 10^{-9} T^{1.75}$ is the bulk diffusivity. A_p (particle surface area) = 20000 m² kg⁻¹, ϵ (char porosity) = 0.41 (-), and ρ_p (particle density) = 1250 kg m⁻³. Finally: $k_g = \frac{D_{bulk}}{R_p}$ is the mass transfer coefficient (m s⁻¹).

4.2 Reaction rates.

Carbon oxidation (from Smith⁷):

$$k_{O_2} = A_{O_2} \exp\left(\frac{-E_A}{RT}\right) \frac{RT A_p \rho_p}{M_C} v_{O_2} \quad (18)$$

Where k_{O_2} (s⁻¹) is the reaction coefficient for carbon oxidation, $A_{O_2} : = 3.01 \times 10^{-2}$ (kgC m⁻² s⁻¹ Pa⁻¹) is the pre-exponential factor, $E_A = 179.4 \times 10^3$ (J mol⁻¹) is the activation energy, R is the universal gas constant in (J mol⁻¹ K⁻¹), T is the temperature (K), and M_C is carbon molecular weight (kg mol⁻¹).

For NO reduction the reaction rate constant of Chan et al² was used, since it is recommended by Visona and Stanmore.⁶

$$k_{NO} = A_{NO} \exp\left(\frac{-E_A}{RT}\right) RT \rho_p \quad (19)$$

And for this reaction $A_{NO} = 3.138 \times 10^4$ (mol NO kg⁻¹ s⁻¹ Pa⁻¹), $E_A = 183.0 \times 10^3$ (J mol⁻¹).

5. Process parameters:

The same process parameters as those considered by Visona and Stanmore⁶ were used:

$\frac{N}{C}$: Nitrogen to carbon atomic ratio in char:

1750 K: (1.0/78.9)(12/14)=0.0109 atoms N/atoms C

1250 K: (1.1/69.9)(12/14)=0.0135 atoms N/atoms C

R_p : Radius of the particle (m): 19×10^{-6}

T=1250, 1500, 1750 K

$C_{NO}^b = 0 - 1500$ ppm

$C_{O_2}^b = 20\%$ v

6. Comparison of the model to Visona and Stanmore's⁶ work.

The model previously outlined was compared to Visona and Stanmore's single particle model.⁶ Although Visona and Stanmore's approach is mostly the same as the present study, two main differences should be noticed:

- Visona and Stanmore did not consider pseudo steady state. Their mass transfer equation is time dependent.

$$\frac{\partial C_i}{\partial t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C_i}{\partial r} \right) = R^v \quad (20)$$

- Whereas, for the model developed in the present work, the effective diffusivity D_e , the particle surface area A_p , and the char porosity ε are considered constant during the char burn-out process, Visona and Stanmore's model did consider variation of these properties. These two distinctions should be taken into account when comparing both models results.

Figure 1 shows the NO concentration profile within a 38 μ m particle, at 1750 K, with $C_{NO}^b = 1000$ ppm and at $C_{O_2}^b = 20\%$. Only the NO reduction was considered, this means that the source terms were switched off. The results from both models are alike, however a slight tendency for lower NO reduction is seen for the analytical solution. This may be explained since Visona and Stanmore's data are for 10% burnout, where their model predicts higher char surface area. This will imply faster NO reduction and therefore the depletion of NO will occur at higher values of r/R .

Figure 1. NO concentration profiles within the particle. Particle size = 38 μ m, $T = 1750$ K, $C_{NO}^b = 1000$ ppm, $C_{O_2}^b = 20\%$. Only NO reduction is considered.

Figure 2 shows the NO profile when only NO production is considered. Although both models predicts the same trend, there is considerably high disagreement in the concentration at $r=0$ for high temperatures (at 1250 K both lines coincide). The difference in the physical properties do not explains the discrepancy between the models, since it only explains slight differences in the slope of the lines, but not on the final value.

A convincing reason that explains why both models predicts the same profile at 1250 K whereas at 1750 K they are off by a factor of 1.8 was not found. The main parameters associated with NO concentration in the center of the particle are $\frac{N}{C}$ (the Nitrogen/Carbon atomic ratio of the char) and ν_{O_2} , the stoichiometric coefficient for carbon-oxygen reaction (mol O_2 mol C^{-1}). Both parameters may vary with temperature. Although in this study the same

parameters as those of Visona and Stanmore⁶ were used, an increase on ν_{O_2} , or a decrease on $\frac{N}{C}$ will lead to agreement between both models.

Figure 2 NO concentration profiles within the particle. Particle size = 38 μ m, T = 1750 K, C_{NO}^b = 0 ppm, $C_{O_2}^b$ = 20 % Only NO production is considered.

Figure 3 presents once more the comparison between the two models, but when both, NO production and reduction were considered. As may be expected, though both models predicts similar trends, there is considerable discrepancy in the absolute values. The explanation for the difference may be a combination of the two ones previously stated: different physical properties, as well as a different interpretation on $\frac{N}{C}$ or ν_{O_2} values. However the real influence of these differences should be considered not only in the NO concentration profile within the particle, but also in the fractional conversion of char-N to NO as will be further discussed.

Figure 3. NO concentration profiles within the particle. Particle size = 38 μ m, $T = 1750$ K, $C_{NO}^b = 0$ ppm, $C_{O_2}^b = 20$ %. NO production and reduction considered.

7. Instantaneous and net conversion of char nitrogen to NO.

Once the NO concentration profile within the particle was determined, the conversion of char-N to NO was computed. The O_2 concentration profile inside the particle was used to determine the conversion vs. time plot. Assuming a shrinking core model:

$$t = -\frac{\rho_p \nu_{O_2} C}{D_e M_c} \int_{R_p|_{r=0}}^{R_p} \frac{1}{\left. \frac{dC_{O_2}}{dr} \right|_{r=R_p}} dR_p \quad (21)$$

Where C is the mass fraction of carbon in the char, $\left. \frac{dC_{O_2}}{dr} \right|_{r=R_p}$ is determined from Equation (10

) and the char conversion x is:

$$x = \frac{R_p^3 - R^3}{R_p^3} \quad (22)$$

Hurt⁸ has experimentally found for a 106-125 μ m particle, at $C_{O_2}^b = 12\%$ and temperatures between 1600-1900 K, that for a char conversion of 28%, 117 ms were needed. The present model at a temperature of 1750K, $C_{O_2}^b = 12\%$ and for a particle of 110 μ m of diameter

predicts, 103 ms for 28% of conversion. This suggests that even with the assumptions made by the model, its predictions are close to experimental values.

The instantaneous conversion of char-N to NO, f_{NO} was defined as the ratio between the moles of NO that leave the particle at time t, and the instantaneous moles of NO that would leave the particle if all char-N were converted to NO, or:

$$f_{NO} = \frac{-4\pi R_p^2 D_e \frac{dC_{NO}}{dr} \Big|_{r=R_p}}{\frac{4\pi R_p^2 D_e \left(\frac{N}{C}\right) dC_{O_2}}{dr} \Big|_{r=R_p}} \quad (23)$$

The net conversion of char-N to NO, F_{NO} represents the ratio between the cumulative moles of NO that leave the particle and the total moles of NO that leave the particle if all char-N were converted to NO.

$$F_{NO} = \frac{-\int_0^t 4\pi R_p^2 D_e \frac{dC_{NO}}{dr} \Big|_{r=R_p} dt}{\frac{4}{3}\pi \left(R_p \Big|_{t=0}\right)^3 \left(\frac{N}{C}\right) \frac{\rho_p C}{M_C}} \quad (24)$$

Figure 4 presents the net char-N conversion to NO vs. char burn-off. The analytical solution predicts almost the same results as those of Visona and Stanmore⁶. The similitude between both lines suggests that the differences between both models, observed in the NO concentration within the particle, may not be so important when considering the char-N conversion to NO. In

fact, from equation (24) it is clear that the value of $\frac{dC_{NO}}{dr} \Big|_{r=R_p}$ is what determines the total

char-N to NO conversion, and from Figure 3 we may see that this value (the slope of the C_{NO} vs. r/R curve) is very similar for both models. The slight discrepancy between both models is more likely due to the fact that Visona and Stanmore considered non-stationary state as well as variable physical properties.

**Figure 4. Net Char-N to NO conversion $T = 1750K$, $C_{NO}^b = 0$, $C_{O_2}^b = 20\%$.
Particle size = $38\mu m$.**

The instantaneous char-N conversion to NO is presented Figure 5. Although Visona and Stanmore⁶ did not present this type of data for their model, a similar trend has been experimentally found by Goel et al⁹ for combustion in a fluidized bed and modeled¹⁰ by the same author at pulverized coal combustion. However in their model, Goel et al⁹ did consider N_2O formation, so comparison is not completely valid.

Figure 5. Instantaneous char-N conversion to NO. $T = 1750K$, $C_{NO}^b = 0$, $C_{O_2}^b = 20\%$. Particle size = $38\mu m$.

Visona and Stanmore⁶ also analyzed the influence of NO bulk concentration on char-N conversion to NO (Figure 6). Both models predicts a decrease in the net char-N conversion to NO when C_{NO}^b is increased. However Visona and Stanmore's⁶ model predicts a higher influence of the bulk concentration on the char-N conversion to NO. Visona and Stanmore's⁶ results are only reported at $T = 1250 K$. Just for comparison, results at $1750 K$ are included.

The effect of particle size is shown by Figure 7. Both models predict in a very similar way a reduction of the char-N conversion to NO as particle size is increased. It should be noticed that the difference between both models is greater when analyzing the incidence of NO bulk concentration, than when analyzing particle size's influence. The fact that Visona and Stanmore⁶ considered variable mass transfer properties, as well as a non steady state seems to be the most probable reason for this discrepancy.

Figure 6. Variation of the char-N conversion to NO with the NO bulk concentration.
Particle size = 38 μ m, $C_{O_2}^b = 20\%$

Figure 7. Variation of the char-N conversion to NO with the particle size.
T = 1750 K, $C_{O_2}^b = 20\%$, $C_{NO}^b = 0$

So far we may conclude that a single particle model for the NO formation at PC combustion conditions was developed based on an analytical solution of the mass transfer balance equation. This model predicts similar trends and results as Visona and Stanmore's⁶ single particle model. There are some differences between both model predictions which may be mainly explained due to the fact that Visona and Stanmore⁶ considered variation in the physical properties with time, whereas the present study did not.

However, since the predictions of the analytical solution agree, at least in a qualitative way, with the experimental results of Goel et al⁹ and Spinti¹¹, and considering its similitude with Visona and Stanmore's⁶ figures, it seems reasonable to use it as a first approach in the interpretation of Spinti's¹¹ results.

8. Application of the model to Spinti's¹¹ data.

In 1997, Jennifer Spinti worked with the University of Utah U furnace and developed a reliable technique for studying the formation of nitrogen oxides (NO_x) during pulverized coal combustion. In her thesis work,¹¹ Spinti focused on the production of NO_x from coal char and she took extreme care to avoid any experimental artifacts.

The uniqueness of Spinti's work is that it is the only one -in the refereed literature- in which chars were obtained and fired at pulverized combustor conditions. Also two different analysis methods (FTIR and chemiluminescent) for measuring the NO_x concentration were used providing added confidence in the results.

Spinti's¹¹ experiments were conducted in a simulated coal environment, which is a mixture of CH₄ (which represents volatile combustion) and char. This allowed the study of char-N conversion to NO_x without any interference from volatile NO_x formation.

This fact, combined with the low particle load (less than 1% by volume) suggests that a particle model, as that previously described, may succeed in modeling Spinti's data. Model's main

assumptions, pseudo-steady state, only CO production during char oxidation, and NO reduction happening only on char surface seem probable considering the high temperature of Spinti's¹¹ experiments (above 2200 K) and the simulated coal environment.

The chars used by Spinti¹¹ had higher ash content and lower carbon content than the chars used in most char-NO reduction studies (Table 1). Therefore, the first step in order to model Spinti's¹¹ results, was to determine the value of k_{NO} (the constant for the NO reduction reaction).

Table 1. Summary of Char-N conversion to NOx from some references.

Ref.	Char source	Ash (%) in char	C ^a (%) in char
Spinti ¹¹	29 kW PC furnace. O ₂ . T=2200-2400K	17.8 - 56.2	40 - 69
Pershing and Wendt ¹²	Gasification Process	20.8	72.8
Wang et al ¹³	N ₂ EFR ^b T=1273 K	2.1-18.4	77.9 - 93.1
Song et al ¹⁴	He. Drop tube reactor. T=1250, 1750 K.	12.1-18.0	69.9 - 78.0
Chan et al ²	Fixed bed reactor. He. T=1273K	14.0	80.5
De Soete ¹⁵	Ar 1500K	N.A.	82.8 - 88.6
Wang et al ¹⁶	He. Wire mesh reactor. T=1000-1800 K.	N.A.	80.5 - 97.4

^a Ultimate analysis (dry)

^b EFR: Entrained Flow Reactor

8.1 Parameter estimation.

The reaction rate constant k_{NO} was determined from a least square optimization of Spinti's¹¹ results. The minimized function, was defined as:

$$\zeta = \sum_{i=1}^N \left(F_{NO}^{\text{exp}} - F_{NO}^{\text{model}} \right)_i^2 \quad (25)$$

Where N is the total number of data points, and F_{NO}^{exp} and F_{NO}^{model} the experimental and model predicted net char-N conversion to NO. Due to the reduced number of data points reported by Spinti (four points for each char at one temperature), k_{NO} was considered as a whole, and it was not split to a pre-exponential factor, and an activation energy value.

The only parameter which was allowed to vary was k_{NO} , all other parameters were found from Spinti experimental data or assumed similar to those reported in the literature. Table 2 presents a brief description of the source of the main parameters used in the model.

Table 2. Parameters used during k_{NO} determination

PARAMETER	SOURCE	Comments
Char oxidation constant	Smith's value, as described by Visona and Stanmore ⁶	
Effective Diffusivity, mass transfer coefficient	Visona and Stanmore ⁶	The pseudo-steady approach did not consider time variation of these properties
O ₂ bulk concentration	Spinti's ¹¹ reported data (3%)	
Particle density	Visona and Stanmore ⁶	Not reported by Spinti ¹¹
Particle diameter	Spinti's ¹¹ experimental particle size distribution.	$D_p = \int_0^1 D_p(x) dx$
Particle surface area	Spinti's ¹¹ experimental N ₂ values.	When available, when not, average of chars
Porosity	Visona and Stanmore ⁶	Not reported by Spinti ¹¹
Pressure	Spinti's ¹¹ measurements (0.84 atm)	
Temperature	Spinti's ¹¹ measurements	The temperature of port 1 were considered since it is where combustion takes place.
Ultimate analysis	Spinti's ¹¹ experimental values	

Before comparing modeled and experimental results, it is worthy to analyze Spinti's data. Figure 8 to Figure 10 represents char-N conversion to NO_x for three different parent coals. The most remarkable trend is the decrease in conversion as NO bulk concentration is increased. This decrease can be split in two regions. At low NO bulk concentration, there is a higher negative slope in the F_{NO} vs. NO bulk concentration curve. This slope becomes less negative, as NO bulk concentration is increased.

Figure 8. Char-N conversion to NO_x for Illinois #6 chars. Data from Spinti¹¹.

Figure 9. Char-N conversion to NO_x for Knife River chars. Data from Spinti¹¹.

Figure 10 Char-N conversion to NO_x for Pittsburgh %8 chars. Data from Spinti¹¹.

Figure 11 - Figure 13 show comparison between model and experimental results for one char of each different parent coal. Plots for all the other chars are presented in Appendix 1. Although the model predicts the same trend of experimental results, it fails in predicting the change in slope already explained. In all but one of the Figures (included those of Appendix 1) there is acceptable agreement between model and experimental data for NO bulk concentrations lower than 400 ppm, however the model underpredicts the conversion at high NO concentrations.

Figure 11. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased.

Illinois #6, Sept. 14,19,20,21. $k_{NO} = 5.10 \times 10^7 \text{ s}^{-1}$

Figure 12. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased.

Knife River, Oct. 31, Nov. 1. $k_{NO} = 1.51 \times 10^7 \text{ s}^{-1}$

Figure 13. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased. Pittsburgh#8 Sept. 25,26,29. $k_{NO} = 1.96 \times 10^7 \text{ s}^{-1}$

The influence of some parameters in the optimization process is shown in Figure 14-Figure 17. It must be clear than these figures do not represent the influence of each parameter in the F_{NO} conversion, but the influence of them on the optimization process. In each case, the optimization process was carried out again, so the optimum k_{NO} was recalculated for each parameter variation.

As it can be seen, the optimization process is not very sensitive to changes on each of the tested parameters. Although there is a slight change in the slope when some parameters (as temperature and particle radius mainly) are changed, it seems unlikely that variations on any of these parameters, between reasonable values, may lead to slopes similar to those presented at high NO bulk concentration.

Figure 14 Effect of particle radius on optimization results.
Illinois#6. Sept. 14,19,20,21.

Figure 15. Effect of temperature on optimization results.
Illinois#6. Sept. 14,19,20,21.

Figure 16. Effect of char surface area on optimization results.
Illinois#6. Sept. 14,19,20,21

Figure 17. Effect of char porosity on optimization results.
Illinois#6. Sept. 14,19,20,21

The effect of k_{NO} in the char-N to NO conversion is presented in Figure 18. Higher values of k_{NO} imply lower F_{NO} when NO bulk concentration is zero. They also imply a more negative slope. A less negative slope is only reached at very low values of k_{NO} for which F_{NO} when NO bulk concentration is zero, will be higher as well. Therefore it is clear that the model is not able to predict the less steep slope at higher NO bulk concentration.

Figure 18. Effect of k_{NO} in the model predictions. Illinois#6. Sept. 14,19,20,21

According to the previous discussion, the process of optimization was performed again, but considering only the first three points at low NO bulk concentration. Figure 19 presents the comparison between model and experimental results when only the three points at low NO bulk concentrations were considered. Results for other chars are presented in Appendix 1. There is an improvement for all chars, and for some chars the lines predicted by the model are almost identical to experimental values.

Figure 19. Comparison between experimental and model predictions (only first three points considered in optimization process). Illinois #6, Sept. 14,19,20,21. $k_{NO} = 6.26 \times 10^7 \text{ s}^{-1}$

8.2 Discussion of model results.

The reason for the discrepancy between model and experimental results at high NO bulk concentration is not clear. Especially if we consider the existence of a coupled mass transfer and kinetics phenomenon. The reduction in F_{NO} with higher NO bulk concentration (despite of the first order for the NO reduction reaction on char surface traditionally reported in literature¹⁷⁻¹⁹) may be explained by a mass diffusion restriction as suggested by Goel et al⁹ for NO formation at fluidized conditions. The lower the NO bulk concentration, the higher the driving force conducting NO outside the particle, and the residence time of NO inside the particle will be lower as well. This will reduce the NO reduction by the char surface, increasing char-N conversion to NO. Higher NO bulk concentration will increase the time NO is inside the particle and the possibility of NO reduction, decreasing F_{NO} . This may be the mass transfer component of the phenomenon. However this might not explain the less negative slope in the curve F_{NO} vs NO at high NO bulk concentration.

One possible explanation may be that at very high NO bulk concentration one can expect a saturation of the active sites where NO reduction takes place. A reduction of the number of these active sites, implies lower NO reduction rate, and therefore higher char-N to NO conversion than that predicted when active sites saturation is not considered. Chambrion et al¹⁹ have recently shown by step response techniques, that the main reaction for NO reduction on the char surface at 850°C is:

Although they consider that NO reduction on NO surface is first order with respect to NO concentration, the initial rate of $C(N)$ formation is a function of NO concentration. Higher NO concentration imply higher N accumulation on char surface (or $C(N)$ formation), and this imply as well higher NO reduction by reaction (26).

In Spinti's experiments, the char C content was low. Therefore, the availability of C for $C(N)$ formation may be limited and at high NO concentration, NO reduction by reaction (26) may have an order different than one, since it will also depend on $C(N)$ concentration.

8.3 Relation between k_{NO} and char properties.

In order to verify the validity of the model, the values of k_{NO} determined by the least square minimization were compared to those of Chan et al.² Figure 20 presents the ratio

$k_{NO}|_{CHAN} / k_{NO}|_{model}$ for Illinois#6, Pittsburgh # 8 and Knife River chars. Although all values are in the same order of magnitude as those of Chan et al.², the difference is as large as five fold for Knife River chars. The values for Illinois#6 chars were closer and those of Pittsburgh #8 in-between. Trying to explain the difference among chars of different coals, we may consider the carbon content of each char. Figure 21 presents the carbon content for the chars which k_{NO} was determined in Figure 20. It is clear that the lower the carbon content, the higher the discrepancy between Chan et al² kinetics and the model predictions. Chan et al² kinetics was determined for

chars with carbon content of 80.5%, therefore it does not seem unreasonable that the chars with more similar carbon content (Illinois #6) have more similar kinetics, and vice versa.

Figure 20. Comparison between k_{NO} predicted by Chan et al² kinetics and k_{NO} predicted by the model for different chars.

Figure 21. Carbon content for the chars used in the model. Data from Spinti.¹¹

Figure 22 presents the relation between the NO reduction reaction constant (k_{NO}) as determined by the optimization routine, and the char carbon content. As it can be seen for Pittsburgh #8 and Illinois #6 chars there is a good correlation between these two variables. The higher the carbon content, the higher NO reduction constant. Even the slopes for Illinois #6 and Pittsburgh #8 lines are very similar. On the other hand, Knife River chars present a different behavior. The reason for this is unclear, although one can argue that at these very low carbon content values a different behavior may be expected and also that only with two points it is questionable to derive any trend.

It is interesting to note that Wang and Thomas¹⁶ found that higher rank coals (higher %C) had a higher NO_x production, also Shimizu et al²⁰ found for combustion in fluidized bed conditions that higher amount of carbon leads to a higher conversion of char-N to NO_x . This may be in disagreement with the previous discussion. However Wang and Thomas¹⁶ explain their results on the basis of higher reactivity (measured as the temperature for 50% char consumption) of low rank coals and not on carbon content itself. Likewise, Shimizu et al²⁰ found a correlation between surface area (not %C) and NO_x production.

Figure 22. Relation between NO reduction constant as predicted by the model and char carbon content.

A different way of representing the relation of Figure 22 is by plotting k_{NO} against char burnout. This is presented in Figure 23. Again there is a good correlation for Illinois #6 and Pittsburgh #8 chars. Higher burn-out represents lower NO reaction rate. This fact has already been reported by Guo and Hecker¹⁸ and Phong-Anant et al.²¹ The first ones observed that the rate of NO_x reduction by char decreases by a factor of three as the carbon conversion increases from 0 to 80%. Phong-Anant et al.²¹ have found during the combustion of chars at pulverized coal combustion, that the conversion of char-N to NO increases with burnout, which may be explained by a decrease on the NO reduction rate.

The reason for the different behavior of Knife River chars is again unclear, but the scarcity of data as well as the very high burnout level may be possible explanations.

Figure 23 Relation between NO reduction constant as predicted by the model and char burnout.

8. Conclusions.

An analytical solution of a simple single particle model for the char-N conversion to NO was developed. This model was in agreement to Visona and Stanmore's⁶ previous model and with general experimental evidence.

Model predictions were compared to Spinti's¹¹ results for the combustion of char in a furnace at PC conditions. The model predicted in a satisfactory way the char-N conversion to NO at low NO bulk concentration. However at high NO bulk concentration, the model underpredicts char-N conversion to NO. The reason for this is still unclear and may be subject of further research.

The value of the rate constant for NO reduction on char surface determined by the model is similar to Chan et al² kinetics for chars with carbon content comparable to those used by Chan et al.² The higher the difference in carbon content between modeled chars and Chan et al² chars, the higher the discrepancy in the rate constant. In the same way there is good correlation between the amount of carbon content and the rate constant for NO reduction on char surface. Higher carbon content implies higher rate constant. Or in an alternative way, higher burnout implies lower reduction rate.

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