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"ADVANCED COMBUSTOR DESIGN CONCEPTS
TO CONTROL NOX AND AIR TOXICS"

SUBMITTED BY

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1.0 Program Overview

Direct coal combustion must be a primary energy source for the electric utility industry and for heavy manufacturing during the next several decades because of the availability and economic advantage of coal relative to other fuels and because of the time required to product major market penetration in the energy field. However, the major obstacle to coal utilization is a set of ever-tightening environmental regulations at both the federal and local level. It is, therefore, critical that fundamental research be conducted to support the development of low-emission, high efficiency pulverized coal power systems.

The University of Utah, Massachusetts Institute of Technology (MIT), Reaction Engineering International (REI) and ABB/Combustion Engineering have joined together in this research proposal to develop fundamental understanding regarding the impact of fuel and combustion changes on ignition stability and flame characteristics because these critically affect: NO_x emissions, carbon burnout, and emissions of air toxics., Existing laboratory and bench scale facilities are being used to generate critical missing data which will be used to improve the NO_x and carbon burnout submodels in comprehensive combustion simulation tools currently being used by industrial boiler manufacturers. to ensure effective and timely transfer of This technology, a major manufacturer (ABB) and a combustion model supplier (REI) have been included as part of the team from the early conception of the proposal.

ABB/Combustion Engineering is providing needed fundamental data on the extent of volatile evolution from commercial coals as well as background information on current design needs in industrial practice. Since they will ultimately be a recipient of the enhanced design methodology, they are also providing ongoing review of the practical applicability of the tools being developed. MIT is responsible for the development of an improved char nitrogen oxidation model which will ultimately be incorporated into an enhanced NO_x submodel. Reaction Engineering International is providing the lead engineering staff for the experimental studies and an overall industrial focus for the work based on their use of the combustion simulation tools for a wide variety of industries. The University of Utah is conducting bench scale experimentation to (1) investigate alternative methods for enhancing flame stability to reduce NO_x emissions and (2) characterize air toxic emissions under ultra-low NO_x conditions because it is possible that such conditions will alter the fate of volatile and semivolatile metal species and the emission of heavy hydrocarbons. Finally the University of Utah is responsible for the development of the improved NO_x and carbon burnout submodels.

2.0 Progress During The Last Quarter

2.1 Solids Sampling System

This study will include bench-scale measurement of the interaction between combustion modifications for NO_x control and the amount of toxic metals in the fine particulate emissions. The majority of the particulate mass is in the larger particles but the fine particles have the greatest environmental consequences. Fine particles travel long distances after emission, cause visible haze, and can be inhaled deep into the lung. The particles less than 1 micron (sub micron particulate) are enriched in volatile metals including lead and arsenic compared to the concentration in the larger particulate.

The objectives for the quarter were to complete the design of a solids sampling system and to purchase a cascade impactor. The system provides the capability of doing experimental work on size-segregated particulate from coal combustion in the aerodynamic

diameter range between 0.4 micron and 10 micron. The experimental work will involve confirmation of model predictions on particle size distribution, metal partitioning, and carbon burnout. The equipment is planned as a modular setup to allow modifying components as needed to meet specific experimental goals.

Key design issues include: extraction of a representative sample from the furnace and minimizing any condensation, coagulation or other particle transformation between the extraction point and the cascade impactor. The dilution must be sufficient to quench the sample to prevent particle growth in the sample line. The flow path must be configured to extract a known sample and to avoid wall loss or other size segregation prior to the impactor. Temperature must remain above the sulfuric acid dew point to prevent condensation on particles in the sample line since the acid mass would change the aerodynamic sizing in the impactor.

The impactor train consists of the following subsystems:

- A water-cooled nitrogen-quenched probe used to extract a sample from the furnace.
- An Andersen "1 ACFM Non-viable Ambient Particle Sizing Sampler". This device has an integral preseparator, 8 stages, and an afterfilter holder.
- The gas handling system including gas drying, on-line gas analysis, metering of sample and dilution flows, optional volatile metals train, and the pump.

Probe Design

The initial probe was designed by Ryan Okerlund based on a modification of a published design (Scotto, 1992). See Figure 1 for details. The probe design criteria were:

1. Achieve isokinetic sampling at furnace conditions using a tip shape that minimizes flow disturbance.
2. Provide a fast quench to 500 °K using dilution nitrogen to stop particle transformation.
3. Maintain the exit gas temperature above the sulfuric acid dew point to avoid including condensed acid as part of the particulate mass during aerodynamic size classification.
4. Provide sufficient cooling to retain the mechanical strength and dimensional stability of the portion of the probe that is exposed to furnace conditions.
5. Keep the probe residence time from the furnace to the impactor short compared to the characteristic time for 0.1 micron particles.
6. Provide the ability to disassemble and clean probe after use in slagging furnace conditions.
7. Be able to modify the probe as needed to validate experimental technique and to meet specific experimental requirements.

The objectives were met by designing a water-cooled outer shell with removable inner sample tube. The tip is interchangeable to allow varying extraction volume flow while

maintaining isokinetic velocity. Dilution nitrogen is supplied to a cluster of injection ports near the tip. Insulation and supplemental electric heating can be provided to avoid excessive cooling of the sample by the surrounding water jacket.

Obtaining an accurate sample of the particle size distribution requires keeping the probe residence time small relative to the characteristic time for the various particle transformation processes. Loss of large particles by gravitational settling and growth of small particles by coagulation were calculated to be the most significant transformation processes for the anticipated experimental conditions. The probe residence time is 0.2 seconds. Table __ shows typical values of the limiting characteristic times.

Transformation Process	Particle Size (microns)	Characteristic Time (seconds)
Gravitational Settling	1	50
	10	0.6
Coagulation	0.1	100
	0.01	2

Table 1
Characteristic Times vs Particle Size

The residence time from the tip to the cascade impactor is approximately 0.2 second. The useful size range for a probe is governed by the ratio of the residence time to the characteristic time for various particle transformation processes. The characteristic time for gravitational settling increases with particle size. For 1 micron particles the settling is not significant but for 10 micron particles the characteristic time is 0.6 second which is comparable to the residence time. The characteristic time for coagulation decreases with decreasing size. For coagulation of 0.01 micron particles the characteristic time is 2 seconds. Coagulation is not a concern since the characteristic time is much greater than the probe residence time even for a particle size smaller than the range of the impactor.

Impactor

The cascade impactor separates the particles by their aerodynamic diameter, that is by the ratio of drag force to inertial force. The particles are deposited on a substrate placed in each stage. The substrates are weighed to determine mass distributions and the collected fractions can be analyzed for composition. The Andersen impactor train can separate particles as follows:

- **Macroparticles:** All particles over 15 microns will be lumped into the preseparator fraction. The macroparticles include the large particles produced by the shrinking core of the original pulverized coal and some fraction of the particles formed by agglomeration of smaller particles.
- **PM10:** Particles less than 10 micron will be separated into 8 fractions with cut sizes of 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4 microns. The PM10 contains the majority of the material which has vaporized, recondensed then grown through coagulation and surface deposition.
- **Submicron Particles:** All particles less than 0.4 micron will be collected as a single afterfilter sample. The submicron particles include the initial products of homogeneous condensation. These highly unstable particles are rapidly

transformed by coagulation and surface reaction and are important for understanding the fundamental mechanisms of metal partitioning.

A limitation of the Andersen impactor is that the entire submicron peak that has been reported in the literature will be represented by the single afterfilter sample. This will limit the ability to study the mechanism of particle condensation and growth. Another limitation is that the preseparator fraction contains all particles larger than 15 micron so the cascade impactor cannot be used to study macroparticles resulting from the original coal. However, a virtual impactor is available to sample these larger particles.

Gas Handling

The gas handling includes supply and flow control of the dilution nitrogen, on-line analysis of the sample gas, metering of sample flow, and the pump. The dilution flow will be measured by spiking the dilution gas with a known concentration of NO. Comparing the NO concentration in the diluted sample to the combustion background and spiked concentration will allow calculation of the dilution ratio and of the sample flow. An existing NOx analyzer is available in the laboratory. All other gas handling components are similar to existing items currently used in the laboratory. The pump, flowmeters and valves will be set up on a rack or cart. See Figure 2 for a schematic arrangement.

2.2 Char Nitrogen Modeling

See Appendix 1

3.0 Plans for Next Quarter

The solids sampling probe will be fabricated and the gas handling equipment will be assembled. Initial measurements in the U Furnace are planned for early summer. NOx studies will also be continuing during the next quarter.

FIGURE 1

ACERC
Solids Sampling Probe
April 20, 1995

FIGURE 2

APPENDIX 1

A Single Particle Model for Studying Char Nitrogen Chemistry at Pulverized Fuel Combustion Conditions

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1 Background

Emission of nitrous and nitric oxides during combustion processes pose a serious threat to the environment. Due to the development of deep staged burners, contribution of volatile nitrogen to NO_x has diminished in significance when compared to the contribution from char nitrogen at pulverized fuel combustion (PFC) conditions. Therefore, an improved char nitrogen model is required to simulate the fate of nitrogen when undergoing combustion conditions. It was hypothesized in the proposal that the char-N formed an intermediate, " $-CNO$ ", which, in turn, lead to NO and N_2O . This mechanism was elucidated from the experimental observations at fluidized bed combustion conditions (FBC). Emission of nitrous oxide (N_2O), though, is significant at FBC conditions, it is negligible at pulverized fuel combustion (PFC) conditions. This due to the fact that most of the N_2O generated at PFC conditions is destroyed due to the homogeneous decomposition in the combustor. Survival of N_2O at low temperature but rapid decomposition at high temperature presents a new path to the formation of free molecular nitrogen. There exist certain operating conditions for char combustion where the conversion of char nitrogen to N_2O is of the same order of magnitude both for the fluidized bed and pulverized fuel conditions. Therefore, analyses of certain physical processes occurring during char combustion at PFC conditions can be studied at FBC conditions.

This report presents a numerical single particle model for the heterogeneous chemistry of NO and N_2O formation which is based on a 15 step kinetic mechanism. The model is used to estimate the kinetic parameters and investigate the operating conditions at which the conversion of char nitrogen to nitrogen oxides both at the PFC and the FBC conditions overlap in magnitudes. The following sections discuss

the heterogeneous chemistry of nitrogen oxide formation, development of the model and the numerical methods investigated to solve the differential equations, sensitivity of char nitrogen conversion to N_2O with respect to model parameters, and the influence of operating conditions on NO and N_2O formation.

2 Heterogeneous Kinetic Mechanism

A 15 step mechanism for NO and N_2O surface kinetics was proposed in an earlier paper [1]. Based on this mechanism an analytical single particle model that used lumped chemistry was developed. However, due to lumping of the reactions, the predictive ability of the analytical model was limited. Therefore, in this report more thorough rate formulations based on the 15 step mechanism are given.

Formation of CO and CO_2

Formation of NO

Destruction of NO and Formation of N_2O

Destruction of N_2O

where, " $-C$ " is a free site and other " $-$ " denote the surface bound species. The mechanism outlined above is tentative and is developed from the experimental observations of [2] and [3]. Table 1 presents

the improved reaction rate formulations of the numerical model discussed in this report. The analytical model [1] uses the equivalent pseudo first order reaction rates obtained by lumping the chemistry of the numerical model.

Table 1: Rate expressions for the numerical model

RATE	NUMERICAL
R_{O_2}	$-\frac{1}{2}k_{O_2}[O_2] - \frac{1}{2}k_{CO}[CO][O_2]^{\frac{1}{2}}$
R_{CO}	$k_{O_2}[O_2] - k_{CO}[CO][O_2]^{\frac{1}{2}}$
R_{CO_2}	$k_{CO}[CO][O_2]^{\frac{1}{2}}$
R_{NO}	$\frac{N}{C}k_{O_2}[O_2]\left(\frac{k_a}{k_a+k_b[NO]}\right) - \frac{N}{C}k_{O_2}[O_2]\left(\frac{k_b[NO]}{k_a+k_b[NO]}\right) - k_{NO_d}[NO] - k_{NO-CO}[NO][CO]$
R_{N_2O}	$\frac{N}{C}k_{O_2}[O_2]\left(\frac{k_b[NO]}{k_a+k_b[NO]}\right) - k_{N_2O_d}[N_2O]$

where, k_i is the reaction rate constant and R_i is the net rate of formation and destruction of species “i”, viz., O_2 , CO , CO_2 , NO , and N_2O . The mechanism proposes that O_2 first reacts with char carbon to form CO and CO_2 . O_2 also breaks the aromatic rings bound to the char surface and forms an active intermediate, I , such as $-CNO$ or $-NCO$. This active intermediate, I , decomposes to form NO or reacts with NO to form N_2O . The fraction $\frac{k_a}{k_a+k_b[NO]}$ as in R_{NO} denotes the probability that the reactive intermediate I forms NO , and $\frac{k_b[NO]}{k_a+k_b[NO]}$ as in R_{N_2O} gives the probability that it reacts with NO to form N_2O . An earlier study [2] has reported that no N_2O is formed in absence of O_2 . Therefore, the N_2O formation term in R_{N_2O} has a dependence on $[O_2]$. The rate expressions for R_{NO} and R_{N_2O} assume a fractional probability of the free $-N$ sites forming NO and N_2O . A single particle numerical model which uses the kinetic rate expressions given in Table 1 is developed in the next section. The rate constants are then determined from the parameter estimation studies.

3 Model Development

The single particle model solves for the diffusive transport and the kinetics of reactants and products in a shrinking char sphere. The model is based on the following assumptions:

1. the char particle is spherically symmetric.
2. the system is in pseudo steady state.

The governing mass conservation equations are:

$$\mathcal{D}_{p_i} \left(\frac{\partial^2 [\cdot]}{\partial r^2} + \frac{2}{r} \frac{\partial [\cdot]}{\partial r} \right) + R_i([\cdot]) = 0 \quad (5)$$

The boundary conditions are

$$@ \quad r = 0 \quad \left. \frac{\partial[\cdot]}{\partial r} \right|_{center} = 0 \quad (6)$$

$$@ \quad r = R_p \quad \mathcal{D}_{p_i} \left. \frac{\partial[\cdot]}{\partial r} \right|_{surface} = k_g([\cdot]_{\infty} - [\cdot]_s) \quad (7)$$

where, $\mathcal{D}_{p_i}$ is the particle diffusivity, and $[\cdot]_{\infty}$ and $[\cdot]_s$ are the concentration of species "i" in the bulk and the particle surface, respectively, k_g is the external mass transfer coefficient, and r is the radial position inside the particle. R_i is the same as defined in Table 1. We have five equations in the form of Equation 5 for five species, *viz.*, O_2 , CO , CO_2 , NO , and N_2O . These five equations, which are second order non-homogeneous ODEs involving non-linear terms are then solved simultaneously using orthogonal collocation on finite elements. This numerical technique is discussed in the next section.

4 Numerical Methods: Orthogonal Collocation on Finite Elements

The system of differential equations described in the previous section can become stiff if the Thiele moduli for the heterogeneous chemistry of nitrogen oxide formation are large such that the kinetic processes are much faster than the diffusive ones. To handle this numerical stiffness a numerical technique is required which is computationally fast, stable, and accurate. Orthogonal collocation on finite elements [5] is one of such techniques used in this study. The following paragraphs give the details of the numerical method.

Consider a porous and spherical char particle undergoing isothermal combustion at pseudo-steady state. Equation 5 can be rewritten in dimensionless form as :

$$\frac{d^2c}{d\xi^2} + \frac{2}{\xi} \frac{dc}{d\xi} + \frac{R_p^2}{\mathcal{D}_p} R(c) = 0 \quad 0 < \xi < 1 \quad \xi = \frac{r}{R_p} \quad (8)$$

$$\frac{dc}{d\xi}(0) = 0 \quad - \frac{dc}{d\xi}(1) = Bi_{mt}(c(1) - 1)$$

where, "c" is the dimensionless concentration. The domain $0 < \xi < 1$, is divided into N_e elements. A new variable $u^l = \frac{\xi - \xi_l}{\Delta \xi_l}$, $\Delta \xi_l = \xi_{l+1} - \xi_l$ is then defined within each element. The interior collocation points are placed at the roots of a legendre polynomial of order N and defined on $0 \leq u^l \leq 1$. The variable u^l goes from zero to one within each element. After applying orthogonal collocation on Eq. 8, the resulting equation at the interior collocation points takes the following form:

$$\frac{1}{\Delta \xi_l^2} \sum_{i=1}^{N+2} B_{ij} c_i^l + \frac{2}{\xi_l + u_i^l \Delta \xi_l} \frac{1}{\Delta \xi_l} \sum_{i=1}^{N+2} A_{ji} c_i^l + \frac{R_p^2}{\mathcal{D}_p} R(c_j^l) = 0 \quad (9)$$

$$l = 1, \dots, N_e; j = 2, \dots, N + 1$$

where, $c_i^l = c(u_i^l) = c(\xi_l + u_i^l \Delta \xi_l)$, and the matrices **B** and **A** approximate the first and the second derivatives. At the boundaries we have the following equations,

$$\frac{1}{\Delta \xi_l} \sum_{i=1}^{N+2} A_{li} c_i^l = 0 \quad (10)$$

$$\frac{1}{\Delta \xi_{Ne}} \sum_{i=1}^{N+2} A_{N+2,i} c_i^{Ne} + Bi_{mt} c_{N+2}^{Ne} - Bi_{mt} = 0 \quad (11)$$

Continuity of the rate term and its first derivative are maintained at the boundaries of the elements instead of collocating at those points.

$$c_{N+2}^l - c_1^{l+1} = 0 \quad (12)$$

$$\frac{1}{\Delta \xi_l} \sum_{i=1}^{N+2} A_{N+2,i} c_i^l - \frac{1}{\Delta \xi_{l+1}} \sum_{i=1}^{N+2} A_{1i} c_i^{l+1} = 0 \quad (13)$$

$$l = 1, \dots, Ne - 1$$

The only unknown in the above equations is the vector of concentrations "c". For a stiff system, this unknown vector is determined by using the Newton - Raphson method. Further details of this method can be found in [5].

Besides orthogonal collocation on finite elements, other methods such as shooting method based on Runge Kutta method with adaptive mesh refinement [6], and the finite volume [7] method were tried, which though were faster but were less robust. This will question their reliability to perform well when the single particle model will be used as a part of the system model.

The next section tests the usefulness of the single particle model by fitting its predictions to the experimental observations. Simultaneously the kinetic parameters are also estimated.

5 Parameter Estimation

The model developed in the previous section was used to obtain the kinetic rate parameters by fitting the model to the experimental data of [3]. The concentration versus time raw data for NO and N_2O were transformed into instantaneous conversion of char nitrogen data as a function of instantaneous particle radius using Equations 14, 15, and 16.

$$f_{NO} = \frac{[NO]}{\frac{N}{C}([CO] + [CO_2])} \quad (14)$$

$$f_{N_2O} = \frac{2[N_2O]}{\frac{N}{C}([CO] + [CO_2])} \quad (15)$$

$$R_p(t) = R_{p0}(1 - X_c(t))^{\frac{1}{3}} \quad (16)$$

where, $R_p(t)$ is the particle radius at any given time and $X_c(t)$ is the conversion of char carbon on mol/mol basis. The numerator of Eq. 14 and 15 represents the molar concentration of NO or N_2O , the denominator represents the rate of consumption of char nitrogen, and N/C is the atomic ratio of nitrogen to carbon in char and represents the proportionality constant for the ratio of rate of nitrogen to carbon consumption during char combustion. The objective function, $\mathcal{L}_2$, minimized was a weighted least square error norm (Equation 17) for the observed and predicted instantaneous conversion data. Minimization of $\mathcal{L}_2$ was done *w.r.t.* the rate constants, *viz.*, k_{O_2} , k_{CO} , k_{NO} , $k_{\text{NO}-\text{CO}}$, $k_{\text{N}_2\text{O}}$, k_2/k_1 , and the effective diffusivity, $\mathcal{D}_p$, of char treated here as a constant during reaction.

$$\mathcal{L}_2 = \left\{ w_{\text{NO}} \sum_j^N (f_{\text{NO}_{exp}} - f_{\text{NO}_{model}})_j^2 + w_{\text{N}_2\text{O}} \sum_j^N (f_{\text{N}_2\text{O}_{exp}} - f_{\text{N}_2\text{O}_{model}})_j^2 \right\}^{\frac{1}{2}} \quad (17)$$

where, N is the total number of data points for a given experimental condition. The f_{NO} and the $f_{\text{N}_2\text{O}}$ profiles exhibit random variation and were used to test the more elaborate chemistry of the model. The search for the optimal parameter values was carried out using the Davidson, Fletcher, Powell [6] optimizer and six experimental data sets (3 temperature of 750, 800, 850°C for each of the two O_2 concentrations of 4 and 8%). The weights w_{NO} and $w_{\text{N}_2\text{O}}$ were chosen in such a way that the search path took minimum CPU time to find the point of minima. Figure 1 shows the comparison for one of the six experimental data sets used for the study. The good agreement between experimental observations and theoretical predictions verifies that the more elaborate kinetic model is able to explain the experimental observations and that it can be used as a predictive tool for other experimental observations. Table 2 shows the optimal values of the rate parameters estimated and their comparison with other values reported in literature [2]. The optimal activation energy for the char oxidation reaction is close to the values reported in [8] for different coal types.

Having developed the model, and estimated the rate parameters our next step was to explore the model performance over a wider range of operating conditions.

6 Model Results and Discussion

One of the primary aims of the single particle model was to test its applicability at pulverized coal conditions. For this purpose, the instantaneous conversions of fuel nitrogen to NO and N_2O were calculated for temperatures ranging from 1750 - 2500 °C and particle size from 2 to 100 μm . A similar analysis was done for fluidized bed conditions where the temperature ranged from 750 to 900 °C and a maximum particle size of 2 mm was used. For the purpose of these studies the model parameters were calculated from the data reported in Table 2.

Figures 2 and 3 show the instantaneous conversion of char nitrogen to NO and N_2O , respectively, as a function of particle size for different temperatures.

The conversion of char nitrogen to NO is of the order of 0.1 - 0.2 for the majority of particle sizes and is in good agreement with the experimental results of Pershing [9]. This agreement gives confidence in the applicability of the single particle model for PFC conditions and the extrapolation of model parameters estimated at FBC conditions to PFC conditions. Furthermore, there is also an overlapping region in which the conversion of char nitrogen to NO during pulverized char combustion is of the same order as during fluidized char combustion. In other words, the conversion of char nitrogen to NO for a large particle and at low temperature is same as that for a small particle and at high temperature. Experiments can be now designed such that the results obtained at FBC conditions can be extrapolated to PFC conditions.

Another interesting observation is that the conversion of char nitrogen to N_2O , is not negligible at PFC conditions. The popular belief is that N_2O is not produced at pulverized char combustion conditions and that char nitrogen is directly oxidized to NO , which, finally gives free molecular nitrogen. This conclusion was derived from the fact that the observed emissions of N_2O are negligible at PFC conditions. Figure 3 shows that this conclusion is not true and that the conversion of char nitrogen to N_2O is significant. At high temperatures (around $2000^\circ C$) the rate of production of N_2O by the reaction of gaseous NO with intermediate species is high. Although at high temperatures the rate of destruction of N_2O is high, a significant amount of N_2O survives due to smaller pore diffusion lengths for smaller particles, characteristic of pulverized fuel combustion. The fact that there is a similar overlapping region between fluidized bed and pulverized fuel combustion conditions suggests that a competition between the diffusion and kinetic mechanisms govern the f_{NO} and the f_{N_2O} ratios. Once N_2O has diffused out of the particle, it is immediately destroyed by the homogeneous decomposition reactions resulting in its low emissions. Since it is difficult to design experiments to study the amount of N_2O (or for that matter NO) formed during char combustion prior to its homogeneous decomposition at high temperatures, models become useful tools in the analyses.

7 Summary

A single particle model is developed which can simulate the experimental conditions ranging from fluidized bed to pulverized fuel combustion conditions. The model predictions at PFC conditions have been compared with the experimental results and are found to be in good agreement. The conversion of char nitrogen to N_2O is not negligible at high temperatures. The low emissions observed are due to further homogeneous decomposition of N_2O and provide an alternate path to free molecular nitrogen formation. The future work will aim at studying the sensitivity of various model parameters. Since CO concentration is critical to the catalytic NO/CO reduction reaction, a boundary layer model for CO oxidation will also be developed.

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8 Figure Captions

Figure 1: Comparison of model predictions with the experimental observations of conversion of char nitrogen to NO and N_2O at a temperature of $800\text{ }^{\circ}C$ and 4% oxygen in helium. The figure shows that the model results are in good agreement with the experimental results.

Figure 2: Model predictions of conversion of char nitrogen to NO both at the PFC and the FBC conditions for 21% oxygen. There is an overlapping region where the conversions are same for both the conditions.

Figure 3: Model predictions of conversion of char nitrogen to N_2O .

Table 2: Comparison of rate constants

Rate Constant (units)	$A \exp(-\frac{E_a}{RT})$	Standard Error	Coal Type	Reference
		$\ln(A)$ and $\frac{E_a}{R}$		
$k_{O_2}(1/s)$	$1.24 \cdot 10^6 \exp(-\frac{6253}{T})$	$(\pm 0.36), (\pm 400)$	Newlands	present work
$k_{CO}(\frac{m^{\frac{3}{2}}}{mol^{\frac{1}{2}} s})$	$1.20 \cdot 10^8 \exp(-\frac{13454}{T})$	$(\pm 0.97), (\pm 1041)$	Newlands	present work
$k_{NO}(1/s)$	$2.09 \cdot 10^8 \exp(-\frac{14455}{T})$	$(\pm 0.79), (\pm 860)$	Newlands	present work
$k_{NO}(\frac{gN}{gCsPa})$	$9.3 \cdot 10^{-1} \exp(-\frac{16900}{T})$	$(-), (-)$	Cedar Grove char (35-50 microns)	deSoete [2]
$k_{NO}(\frac{gN}{gCsPa})$	$1.2 \cdot 10^0 \exp(-\frac{16600}{T})$	$(-), (-)$	Prosper char (35-50 microns)	deSoete [2]
$k_{NO}(\frac{gN}{gCsPa})$	$5.8 \cdot 10^0 \exp(-\frac{17800}{T})$	$(-), (-)$	Eschweiler char (35-50 microns)	deSoete [2]
$k_{NO-CO}(\frac{m^3}{mol s})$	$3.68 \cdot 10^7 \exp(-\frac{13097}{T})$	$(\pm 1.11), (\pm 1083)$	Newlands	present work
$\frac{k_2}{k_1}(\frac{m^3}{mol})$	$9.0 \cdot 10^2 \exp(-\frac{3551}{T})$	$(\pm 0.16), (\pm 171)$	Newlands	present work
$k_{N_2O}(s^{-1})$	$4.8 \cdot 10^8 \exp(-\frac{16983}{T})$	$(\pm 0.764), (\pm 818)$	Newlands	present work
$k_{N_2O}(\frac{gN}{gCsPa})$	$0.68 \exp(-\frac{12200}{T})$	$(-), (-)$	Prosper char	deSoete [2]
$k_{N_2O}(\frac{gN}{gCsPa})$	$0.9 \exp(-\frac{13900}{T})$	$(-), (-)$	Cedar char	deSoete [2]
$k_{N_2O}(\frac{gN}{gCsPa})$	$0.14 \exp(-\frac{10000}{T})$	$(-), (-)$	Eshweiler char	deSoete [2]

Fig. 1

Fig. 2

Fig. 3.