A comprehensive kinetic mechanism is proposed for the release of char-bound nitrogen in coal (char-N) into the gas phase during the combustion of coal char particles. The salient feature of the proposed mechanism is that char-N is converted competitively to NH$_3$ as well as to NO at the surface of the particles. Based on the proposed kinetic mechanism, a mathematical model is developed for the transient formation of char-NO originated from char-N during the combustion of a single particle of coal char in an O$_2$/Ar stream.

The theoretical predictions of the model are compared with the experimental data for three kinds of chars, of which the parent coals are Taisei (anthracite, China), Taiheiyo (non-caking bituminous, Japan) and an activated sludge (a pseudo low-rank coal from waste-water treatment): their fuel ratios range from 0.12 to 4.16.

Quantitative agreement is found between the predictions of the model and the measured values for the transient formation of char-NO and for the overall fractional conversion of char-N into char-NO. This proposed mathematical model, based on a comprehensive kinetic mechanism, is recommended for modeling the char-NO formation step in practical coal combustors.

**Introduction**

Considerable effort has been devoted to the kinetic mechanism of char-NO formation from char-bound nitrogen in coal (char-N). The pioneering works by Pohl and Sarofim$^1$, Beer and Martin$^2$ and Pershing and Wendt$^3$ resulted in the experimental distinction of char-NO from volatile-NO formed from volatile nitrogen compounds such as NH$_3$ and HCN.

Theoretical approaches to the prediction of the fate of char-N during combustion have been based on many experimental studies. Wendt and Schulze$^4$, prior to the above-mentioned experimental work, proposed a model in which char-N is converted to NO at the particle surface, and further reaction to N$_2$ occurs homogeneously either in the pores or in the gas film surrounding the particle. The predictions of their model compare qualitatively with trends observed in later experiments. However, little attention has been directed to the ability of the model to account for the mutual effects of the main combustion reaction, i.e. C + 1/2 O$_2$ = CO, and the concurrent heterogeneous and homogeneous reactions related to char-NO formation. In addition, there have been no actual concrete comparisons between the predictions of the model and the experimental data. In general, the rate of combustion of coal char has been observed to be strongly dependent on the parent coal. Therefore, a model applicable to the mathematical prediction of NO formation in practical coal combustors must account for the characteristic combustibility of the chars in
Char-NO formation. Such a model has not yet been perfected. Indeed, our recent data for char-NO formation from a particle of coal char cannot be described by any existing model.

The objective of the present study is to develop a mathematical model for char-NO formation during the combustion of a single particle of coal char. First, a comprehensive kinetic mechanism including char carbon (char-C) and char hydrogen (char-H) is proposed for the release of char-N into the gas phase. The primary feature which distinguishes the proposed kinetic mechanism from prior ones is that char-N is converted competitively to $\text{NHi}$, as well as to NO at the surface of the particle during the entire combustion period. Next, a mathematical model for the proposed kinetic mechanism involving 4 heterogeneous gas-solid reactions and 21 homogeneous gas-phase reactions is developed to describe the transient formation of char-NO during the combustion of a single particle of coal char.

### 1. Theoretical Analysis

#### 1.1 Kinetic mechanism

Twenty-five heterogeneous and homogeneous reaction steps have been introduced in the present theoretical analysis of the overall formation of char-NO during the combustion of a single particle of coal char in an $\text{O}_2$/Ar stream. These mechanisms are summarized in Table I together with the rate constants and references.

1. Heterogeneous gas-solid reactions: The proposed reaction mechanisms for the heterogeneous combustion of char are shown schematically in Fig. 1. Reactions R1 and R4 have already been used in existing kinetic models.\textsuperscript{4,6}

2. Homogeneous gas-phase reactions: Reactions R5 through R25 are postulated to occur outside of the char particle. The rate expressions and the rate constants for reactions R5 to R7 in Table I have been taken from Howard, et al.\textsuperscript{7}, Baulch, et al.\textsuperscript{8} and Chan, et al.\textsuperscript{9}, respectively. Reactions R8 to R25 have been derived from the full kinetic model\textsuperscript{10} for the gas-phase reaction in an NH$_3$-H$_2$-NO-$\text{O}_2$-Ar mixture, but the elementary reactions involving either NH$_3$ or NH$_2$ have been excluded.

#### 1.2 A mathematical model for the overall formation of char-NO

A mathematical model was developed to describe the formation of char-NO during the combustion of a single particle of coal char. The following assumptions are made:

1. The reacting system (Fig. 2) is isothermal. The number of coal-char particles on the porous plate is small so that the effect of the neighboring particles on char-NO formation can be ignored.

2. Since the chars were prepared by pyrolysis at a temperature about 100 K higher than the combustion temperature, no volatile NO is formed and since N$_2$-free oxidizing gas is used, no thermal-NO is formed.

3. Spherical symmetry and a pseudo steady-state are assumed throughout the combustion period. This postulate is applicable because the maximum temperature drop ratio across the particle does not exceed 0.03 for the reaction conditions\textsuperscript{11}.

4. No gas-phase formation and reduction of char-NO occurs within intraparticle pores.

5. The gaseous products (NO, NH, H$_2$O and CO) evolved from the particle mix instantaneously and perfectly with the $\text{O}_2$/Ar stream at $z = 0$ in Fig. 2.
TABLE I

Heterogeneous and homogeneous mechanisms of reaction employed in this work

<table>
<thead>
<tr>
<th>heterogeneous gas-solid reaction</th>
<th>rate expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 C + 1/2 O₂ = CO</td>
<td>Eq.(2)</td>
<td>Wendt &amp; Schulze(1976)</td>
</tr>
<tr>
<td>R2 H + 1/4O₂ = 1/2H₂O</td>
<td>Eq.(8)</td>
<td>this work</td>
</tr>
<tr>
<td>R3 NH(s) = NH(g)</td>
<td>Eq.(10)</td>
<td>this work</td>
</tr>
<tr>
<td>R4 N + 1/2O₂ = NO</td>
<td>Eq.(9)</td>
<td>Wendt &amp; Schulze(1976)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>homogeneous gas-phase reaction</th>
<th>rate expression and rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>R5 CO + 1/2O₂ = CO₂</td>
<td>$-r_{CO} = 1.3 \times 10^{14} (H₂O)^{1/2} (CO)(O₂)^{1/2} \exp(-125.5/RT)$</td>
</tr>
<tr>
<td>R6 CO + OH = CO₂ + H</td>
<td>$\ln k_b = 10.847 + 3.995 \times 10^{-4}T$ Howard et al. (1973)</td>
</tr>
<tr>
<td></td>
<td>$k_b = 1.5 \times 10^{-3} \exp(-167.2/RT)$ [mol/cm²/s] Baulch et al. (1976)</td>
</tr>
<tr>
<td>R7 CO + NO = 1/2 N₂ + CO₂</td>
<td>$k_{iii} = 2.08 \times 10^{-4} \exp(-108.7/RT)$ [mol/cm²/s/kPa] Chan et al. (1983)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$k^* = A T^\alpha \exp(-E/RT)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [cm³, moles, s]</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>R8 NH + O₂ = NO + OH</td>
<td>$1.0 \times 10^{10}$</td>
</tr>
<tr>
<td>R9 NH + O₂ = HNO + O</td>
<td>$1.0 \times 10^{12}$</td>
</tr>
<tr>
<td>R10 NH + NO = N₂ + OH</td>
<td>$1.0 \times 10^{13}$</td>
</tr>
<tr>
<td>R11 NH + OH = NO + H₂</td>
<td>$1.6 \times 10^{12}$</td>
</tr>
<tr>
<td>R12 HNO + OH = NO + H₂O</td>
<td>$3.6 \times 10^{13}$</td>
</tr>
<tr>
<td>R13 HNO + M = H + NO</td>
<td>$3.0 \times 10^{16}$</td>
</tr>
<tr>
<td>R14 H + O₂ = OH + O</td>
<td>$2.24 \times 10^{14}$</td>
</tr>
<tr>
<td>R15 O + H₂ = OH + H</td>
<td>$1.8 \times 10^{10}$</td>
</tr>
<tr>
<td>R16 H₂ + OH = H₂O + H</td>
<td>$1.17 \times 10^{9}$</td>
</tr>
<tr>
<td>R17 OH + OH = H₂O + O</td>
<td>$6.3 \times 10^{12}$</td>
</tr>
<tr>
<td>R18 H₂ + M = H + H + M</td>
<td>$2.23 \times 10^{12}$</td>
</tr>
<tr>
<td>R19 OH + H + M = H₂O + M</td>
<td>$2.2 \times 10^{22}$</td>
</tr>
<tr>
<td>R20 N + OH = NO + H</td>
<td>$4.1 \times 10^{13}$</td>
</tr>
<tr>
<td>R21 N + O₂ = NO + O</td>
<td>$6.4 \times 10^{7}$</td>
</tr>
<tr>
<td>R22 N + NO = N₂ + O</td>
<td>$1.55 \times 10^{13}$</td>
</tr>
<tr>
<td>R23 N + O + M = NO + M</td>
<td>$6.44 \times 10^{16}$</td>
</tr>
<tr>
<td>R24 N + N + M = N₂ + M</td>
<td>$1.55 \times 10^{17}$</td>
</tr>
<tr>
<td>R25 O + O + M = O₂ + M</td>
<td>$1.9 \times 10^{15}$</td>
</tr>
</tbody>
</table>

6). The 14 gaseous chemical species: CO₂, CO, N₂, O₂, H₂, NO, H₂O, HNO, NH, OH, H, O, N, and Ar, are assumed to be ideal gases.

7). The fluid has a uniform velocity distribution (plug flow).

The basic differential equations describing mass transfer and chemical reaction can be derived from the above assumptions as follows:

**Heterogeneous char combustion**

For the pseudo steady-state hypothesis, the overall rate of oxidation of char-C in a spherical particle of char can be expressed as

$$D_e \left( \frac{\partial^2 C_{O}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{O}}{\partial r} \right) = \frac{\xi \rho_p R_C}{M_C}$$

(1)

where

$$R_C = - \frac{dW_C}{d\theta} = (\eta A_t + A_s) k_1 P_O$$

(2)

Here $R_C$ is the overall rate of reaction of char-C on a mass basis and $k_1$ is the intrinsic reaction rate constant on an area basis [g-C/cm²/s/kPa].

The initial and boundary conditions are:
The effective diffusivity, $D_e$, can be estimated using the following relation derived from Bosanquet's equation:

$$D_e = \frac{1}{(1/D_{K,O_2}) + (1/D_{O_2-Ar})}$$

where $D_{K,O_2}$ and $D_{O_2-Ar}$ are the Knudsen and molecular diffusivities, respectively, of $O_2$. The values of $D_{K,O_2}$ and $D_{O_2-Ar}$ can be estimated from the literature. In the present work, the value of $p$ is assumed to be 2.0. The effectiveness factor, $\eta$, in Eq. (2) can be also calculated from the existing theory.

The mass transfer coefficient at the particle surface, $h_D$, can be obtained from

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}.$$  

Based on the kinetic mechanism shown in Fig. 1, the overall rates of release of char-N, char-H and char-NH into the gas phase can be expressed as follows:

$$R_N = - \frac{dW_N}{d\theta} = (1-\gamma)\frac{W_N}{W_c} R_C$$

$$R_{NH} = - \frac{dW_{NH}}{d\theta} = \gamma\frac{W_N}{W_c} R_C.$$  

**Homogeneous gas-phase reaction**

The target chemical species and other reactants and products are labelled $Y_k$, $R_i$, and $P_j$, respectively. The mechanism of the elementary reactions of $N$ are related to the species $Y_k$ as follows:

$$R_{i,+} + R_{i,-} + R_{i,3} \rightarrow P_{i+} + P_{i-} + Y_i$$

where $k_{i,+}$ and $k_{i,-}$ are the forward and reverse rate constants, respectively, for the $i$-th reaction.

The equation for the conservation of species $Y_k$ is

$$\frac{\partial C_{Y_k}}{\partial \theta} + u \frac{\partial C_{Y_k}}{\partial z} = \sum_{i=1}^{N} \left( k_{i,+} C_{R_{i,+}} C_{R_{i,-}} C_{R_{i,3}} - k_{i,-} C_{P_{i+}} C_{P_{i-}} C_{Y_k} \right)$$

where $C_{Y_k}$ is the concentration of $Y_k$ [mol/cm$^3$]. The equations of conservation for the species to be analyzed ($Y_1, Y_2, \ldots, Y_m$) can be introduced similarly.
The initial conditions for $\theta = 0$ and all values of $z$ are

$$C_{O_2} = C_{O_2,0}, \quad C_{Ar} = C_{Ar,0}$$

$$C_{V_k} = 0 \text{ (except for } O_2 \text{ and } Ar)$$

Using assumption (5), the boundary conditions for $CO$, $NO$, $NH$, $H_2O$, $O_2$ and $Ar$ are:

For $\theta > 0$ and $z = 0$;

$$C_{CO} = \frac{1}{RT_c} \left[ I + \frac{(B/RC)(MH/Mc)}{R_C} \right]$$

$$C_{NO} = \frac{1}{RT_c} \left[ I + \frac{(B/RN)(MH/Mc)}{R_N} \right]$$

$$C_{NH} = \frac{1}{RT_c} \left[ I + \frac{(B/RNH)(MNH/Mc)}{R_NH} \right]$$

$$C_{H_2O} = \frac{1}{2RT_c} \left[ I + \frac{(B/RQ)(MH/MC)}{R_Q} \right]$$

$$C_{O_2} = C_{O_2,0} - \frac{(C_{CO} + C_{NO} + C_{H_2O})}{2}$$

and

$$C_{Ar} = \frac{P_T}{RT_c} \left[ C_{CO} + C_{NO} + C_{NH} + C_{H_2O} + C_{O_2} \right]$$

where

$$B = \frac{u_g \rho_g A_T (a_A + a_z)(M_A/M_w)}{4 \pi r_n^2}$$

and

$$M_w = \left( \frac{RT_c}{P_T} \right) (M_{Ar} C_{Ar,0} + M_{O_2} C_{O_2,0})$$

$P_T = 101.3$ kPa and $n$ is the total number of the char particles on the porous plate.

The boundary conditions for the other species are

$$C_{V_k} = 0 \text{ for } \theta > 0 \text{ and } z = 0$$

By solving these simultaneous differential equations numerically the time-change in the concentration of $NO$ at $z = Z$ can be predicted. In addition, the overall fractional conversion of char-$N$ into char-$NO$, $\eta_{NO}$, can be obtained by integrating the concentration of $NO$ with respect to time over the entire combustion period.

2. Experimental

2.1 Coal-char Samples

In this study, three ranks of parent coals were employed: Taisei (anthracite coal from China; fixed carbon $= 79.3\%$; volatile matter $= 9.2\%$; moisture $= 1.1\%$; and ash $= 10.4\%$), Taiheiyo (non-caking bituminous coal from Japan, FC $= 40.0\%$, VM $= 45.0\%$, M $= 4.1\%$, ash $= 10.9\%$); and activated sludge (a pseudo low-rank coal from waste-water treatment, FC $= 11.7\%$, VM $= 48.7\%$, M $= 1.7\%$, ash $= 37.9\%$). Their fuel ratios (VM/FC) vary between 0.12 and 4.16. The coal particles were devolatilized before the experiments in a stream of N$_2$ at the temperatures of 1273, 1373 and 1473 K ($T_D$) to produce samples of coal-char particles. The ultimate analyses of parent coals and their chars are summarized in Table II together with the fuel ratios of the parent coals. Figure 3 shows the experimentally determined relationship between the complete combustion time, $\theta$, of a single char particle with an initial diameter, $d_0$, measured in an $O_2$-Ar stream. It is evident from this figure that the chars employed in this work have very different rates of combustion.

2.2 Experimental apparatus and procedure

Figure 4 shows the experimental apparatus and Fig. 5 gives the details of the main reaction vessel. The quartz inner tube (41 mm in diameter) is attached with bolts and sealed with silicon-rubber packing in the outer tube (60 mm in diameter), which has a sintered porous quartz plate on its bottom. The apparatus itself is essentially a radiative electric furnace with a SiC heater. The main reaction vessel was placed at the center of this furnace and the wall temperature of the reaction tube was maintained steady and uniform throughout the whole combustion period. The $O_2$/Ar mixture used as an oxidizer was preheated to a predetermined combustion temperature ($T_c$) by an electric heater.

Prior to the combustion experiments, weighed particles of char (0.02 - 5 g) were placed on the porous plate in an Ar stream ($O_2$-free). After confirming that isothermal, steady-state conditions existed over the entire section of the reaction vessel, the Ar gas was rapidly replaced by an $O_2$/Ar mixture. The time-change of the concentration of $NO$ at $z = Z$ was measured continuously by a high-order derivative spectro-photometer (Yanagimoto Co. Ltd., UO-1 type). Concentrations of $NO_2$, HCN and $NH_3$ were also measured but were found to be negligibly small as compared to the $NO$ concentration.

3. Results and discussion

3.1 Determination of intrinsic gas-solid reactivities and physical properties

The intrinsic rate constants, $k_i$, of the char particles (except for the activated-sludge char) were first measured using a high-temperature
TABLE II
Ultimate analyses of coal chars and their parent coals and the fuel ratio (=VM/FC) of the parent coals

<table>
<thead>
<tr>
<th></th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>N (wt %)</th>
<th>Fuel Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Sludge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>char (1273K)</td>
<td>22.17</td>
<td>4.28</td>
<td>4.60</td>
<td>4.16</td>
</tr>
<tr>
<td>&quot; (1373K)</td>
<td>16.62</td>
<td>0.16</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>14.52</td>
<td>0.12</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>14.31</td>
<td>0.09</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Taiheiyo coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>char (1273K)</td>
<td>67.86</td>
<td>5.71</td>
<td>1.35</td>
<td>1.13</td>
</tr>
<tr>
<td>&quot; (1373K)</td>
<td>63.40</td>
<td>0.41</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>62.39</td>
<td>0.29</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>61.60</td>
<td>0.18</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>Taisei coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>char (1273K)</td>
<td>79.11</td>
<td>2.61</td>
<td>0.90</td>
<td>0.12</td>
</tr>
<tr>
<td>&quot; (1373K)</td>
<td>75.60</td>
<td>0.43</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>74.99</td>
<td>0.85</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>&quot; (1473K)</td>
<td>74.09</td>
<td>0.34</td>
<td>0.59</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Complete combustion-time of a single particle of coal char

TGA unit (Rigaku Electric Work Ltd., Model A-10377). Details of the method of measurement and of the determination of the rate constant of an activated-sludge char are given in a previous paper.15

The measured values of $k_1$ for the Taisei and Taiheiyo coal chars are, $k_1 = 3.21 \times 10^{-3}$ exp ($-53.9/RT$) and $3.04 \times 10^{-5}$ exp ($-52.6/RT$), respectively, for the following ranges of experimental conditions: $T = 950 - 1280$ K, $d_0 = 180 - 1125\mu$m, $O_2 = 3 - 10$ vol%.

Other properties used in the calculation were determined experimentally or estimated from the literature. Some important properties are:

<table>
<thead>
<tr>
<th>parent coal</th>
<th>Taisei coal</th>
<th>Taiheiyo coal</th>
<th>Activated sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk density of particle</td>
<td>$\rho_p \text{ [g/cm}^3\text{]}$</td>
<td>1.25–1.4</td>
<td>0.68–0.8</td>
</tr>
<tr>
<td>porosity</td>
<td>$\varepsilon_s$</td>
<td>0.15–0.23</td>
<td>0.35–0.55</td>
</tr>
<tr>
<td>specific internal surface area</td>
<td>$A_I \text{ [m}^2\text{/g]}$</td>
<td>5–10</td>
<td>15–20</td>
</tr>
</tbody>
</table>

3.2 Complete combustion time of a single particle of char

The calculated and the experimental results for the complete combustion time, $\theta_D$, of a single particle of char compared confirm the validity of the theoretical model. The calculated values of $\theta_D$ based on Eqs. (1) and (2) were in good agreement with the measured complete combustion time for the three kinds of coal-char particles (Fig. 3).

3.3 Determination of $\gamma^*$

Before determining $\gamma^*$ as the most important characteristic parameter of the present kinetic model, the data for a single particle of char must be extracted from the data for a cluster of particles. Figure 6 shows the experimental relationship between $\eta_{NO}$, the overall fractional conversion of char-N to char-NO, and $A_p/A_T$, the apparent number of layers of packed particles. Here $A_p = (\pi/4)d_0^2$ and $A_T$ is the cross-sectional area of the reaction tube. $\eta_{NO}$ increases with a decrease in the value of $A_p/A_T$ and finally becomes constant for $A_p/A_T < 0.08$, as seen in Fig. 6. The formation data of the NO for $A_p/A_T <$
0.08 are thus presumed to approximate those of a single particle of char. As a result, the following data for the formation of char-NO are limited to conditions satisfying this criterion.

Figure 7 shows a typical example of the measured transient formation of char-NO during combustion. In this figure, the experimental curve for NO is compared with the calculated curves obtained with \( \gamma \) as a parameter.
i.e., \( \gamma^* \)). For increasing values of \( \gamma \), the theoretical curve is expected to approach the experimental one, coinciding at a certain value of \( \gamma \). To determine the proper value of \( \gamma^* \) to be used in the development of the proposed model, the ratio of the calculated time-integrated formation of NO to the experimentally determined one is plotted against \( \gamma \) (Fig. 8). The values of \( \gamma^* \) can thus be determined graphically. The \( \gamma^* \)-value thus obtained is likely to be strongly related to the initial mass ratio of char-C to char-N, \( (W_c/W_N) \), as can be inferred from Fig. 9, which also includes the data for the combustion of char particles in a packed bed.\(^{16}\)

### 3.4 Transient formation of char-NO during combustion

Figures 10 and 11 are typical examples of the comparison of the experimental data with the calculated results for the transient formation of char-NO during the combustion of a single particle of char, with the value of \( \gamma^* \) estimated from Fig. 9. As shown in these figures, the present kinetic model describes the transient formation of char-NO over the entire period of combustion, including the effects of the characteristic combustibilities of the chars (Fig. 3) and of the initial diameter of the particle. This good agreement between the calculated and the experimental results was confirmed over the following range of combustion conditions: \( T_c = \...\)
973–1173 K, $T_p = 1273–1473$ K, $d_0 = 180–1125$ μm and $O_2 = 3–10$ vol.%. 

3.5 Overall fractional conversion of char-N into char-NO

The predictions of the present model are compared with the measured overall fractional conversion of char-N into char-NO (Fig. 12) to fully demonstrate the potential of the comprehensive kinetic mechanism used in the model. The experimental values of $\eta_{NO}$ decrease according to the rank of the parent coal in the order Taisei coal, Taiheiyo coal and activated sludge. A similar trend has been observed experimentally by several investigators. However, the theoretical approach to this subject is definitely limited. For a single particle, the predictions of the present model compare favorably with the measurements in Fig. 12.

![Table showing char-N conversion](image)

Fig. 12. Overall fractional conversion of char-N into char-NO over the entire period of combustion

Conclusions

A mathematical model based on a comprehensive kinetic mechanism has been developed for the formation of char-NO during the combustion of a single particle of coal char. The predictions of this model agree closely with the experimental results for the overall fractional conversion of char-N into char-NO as well as for the transient formation of char-NO during the entire combustion period. Comparison of the experimental data for three kinds of coal chars, of which the parent coals have a fuel ratios between 0.12 and 4.16, has shown that the present model can describe well the effect of the combustibility of the char on the formation of char-NO.

Nomenclature

$A = \text{frequency factor}$

$A_e = \text{specific external surface area of particle} [\text{cm}^2/\text{g}]$

$A_i = \text{specific internal surface area of particle} [\text{cm}^2/\text{g}]$

$C_i = \text{concentration of i-species} [\text{mol/cm}^3]$

$C_{O_2,H_2} = \text{bulk concentration of oxygen} [\text{mol/cm}^3]$

$D_e = \text{effective diffusivity} [\text{cm}^2/\text{s}]$

$D_{K-O_2} = \text{Knudsen diffusivity} [\text{cm}^2/\text{s}]$

$D_{O_2-Ar} = \text{molecular diffusivity} [\text{cm}^2/\text{s}]$

$d_0 = \text{initial diameter of char particle} [\text{cm}]$

$E = \text{energy of activation} [\text{kJ/mol}]$

$h_D = \text{mass transfer coefficient} [\text{cm}/\text{s}]$

$k_1 = \text{intrinsic rate constant on area basis for oxidation of char-C} [\text{g-C/cm}^2/\text{s}/\text{kPa}]$

$k^+, k^- = \text{forward and reverse rate constant, respectively, for a homogeneous gas-phase reaction}$

$M_i = \text{molecular weight of i-species} [\text{g/mol}]$

$n = \text{total number of char particles in the packed bed}$

$P_i = \text{partial pressure of i-species} [\text{kPa}]$

$P_T = \text{total pressure} [\text{kPa}]$

$R = \text{universal gas constant} [\text{cm}^3\text{kPa}/\text{mol}\text{K}, \text{kJ/mol}\text{K}]$

$Re = \text{Reynolds number for the particle}$

$R_j = \text{overall rate of release of the j-component of the char} [\text{g}/\text{g/s}]$

$r = \text{radial distance from the center of the particle} [\text{cm}]$

$Sc = \text{Schmidt number}$

$Sh = \text{Sherwood number}$

$T_c = \text{combustion temperature} [\text{K}]$

$T_p = \text{pyrolysis temperature} [\text{K}]$

$u_g = \text{linear velocity of reactant gas} [\text{cm/s}]$

$W_j = \text{mass concentration of j-component of the char} [\text{g/g}]$

$Z = \text{distance from porous plate to point of gas sampling} [\text{cm}]$

$z = \text{distance from porous plate} [\text{cm}]$

Greek symbols

$\beta^* = \text{characteristic parameter of the proposed kinetic model}$

$\gamma = \text{parameter of calculation}$
\( \gamma^* \) = characteristic parameter of the proposed kinetic model

\( \varepsilon \) = porosity of a particle of char

\( \zeta \) = stoichiometric coefficient for reaction R1

\( \eta \) = effectiveness factor

\( \eta_{NO} \) = overall fractional conversion of char-N into char-NO

\( \Theta \) = dimensionless reaction time \((\theta/\theta_0)\)

\( \theta \) = reaction time \([\text{min}, \text{s}]\)

\( \theta_D \) = complete combustion time of a single particle of char \(\text{[min}, \text{s}]\)

\( \rho_B \) = bulk density of a particle of char \([\text{g/cm}^3]\)

\( \rho_x \) = density of reactant gas \([\text{g/cm}^3]\)

**Subscript**

0 = initial

**REFERENCES**


