

A COMPREHENSIVE KINETIC MODEL FOR THE FORMATION OF CHAR-NO DURING THE COMBUSTION OF A SINGLE PARTICLE OF COAL CHAR

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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 Sarofim¹, Beer and Martin² and Pershing and Wendt³ 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 Schulze⁴, 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. $\text{C} + 1/2 \text{O}_2 = \text{CO}$, 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 data⁵ 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 NH_i , 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. The theoretical predictions of this model are compared with the experimental data for three kinds of coal char whose parent coals are Taisei (anthracite, China), Taiheiyo (non-caking bituminous, Japan), and an activated sludge (a pseudo low-rank coal from waste-water treatment). The combustion characteristics of these chars differ significantly from one another, as will be shown. Finally, the validity of the proposed model is examined by comparing the experimental and the calculated results for the transient formation of char-NO and for the fractional conversion of char-N into char-NO during combustion, for chars of different rank parent coals.

To avoid the formation of thermal-NO, a mixture of O_2 and Ar was employed as the oxidizer. In addition, all of the chars were prepared by pyrolysis at a temperature about 100 K higher than that for combustion, in order to minimize the effect of volatile matter on char-NO formation.

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 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.^{4,6} The key mechanism in the present model is reaction R3, which has not previously been considered. The salient hypothesis is that a mass fraction γ^* of the total char-N is released into the gas phase in the form of NH_i . The hydrogen in NH_i is compensated for by the fraction $(1-\beta^*)$ of the total char-N. [NH_i is represented by NH to simplify the theoretical approach.] The residual fraction of char-N, $(1-\gamma^*)$, and of char-H, β^* , are oxidized to NO and H_2O , respectively. The values of γ^* and β^* are characteristic parameters related to the combustibility of the chars. At the present stage, both must be determined experimentally, but fortunately the value of β^* can be obtained from the mass balance: $\beta^* = 1 - (\gamma^*/14)$ (W_N/W_H), provided γ^* can be determined independently.

(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.⁷, Baulch, et al.⁸ and Chan, et al.⁹, respectively. Reactions R8 to R25 have been derived from the full kinetic model¹⁰ for the gas-phase reaction in an $\text{NH}_3\text{-H}_2\text{-NO-O}_2\text{-Ar}$ 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 conditions¹¹.
- 4). No gas-phase formation and reduction of char-NO occurs within intraparticle pores.
- 5). The gaseous products (NO, NH , H_2O and CO) evolved from the particle mix instantaneously and perfectly with the O_2/Ar stream at $z = 0$ in Fig. 2.

TABLE I
Heterogeneous and homogeneous mechanisms of reaction employed in this work

heterogeneous gas-solid reaction	rate expression	Reference
R1 $C + 1/2 O_2 = CO$	Eq.(2)	Wendt & Schulze(1976)
R2 $H + 1/4O_2 = 1/2H_2O$	Eq.(8)	this work
R3 $NH(s) = NH(g)$	Eq.(10)	this work
R4 $N + 1/2O_2 = NO$	Eq.(9)	Wendt & Schulze(1976)
homogeneous gas-phase reaction	rate expression and rate constant	
R5 $CO + 1/2O_2 = CO_2$	$-r_{CO} = 1.3 \times 10^{14} (H_2O)^{1/2} (CO)(O_2)^{1/2} \exp(-125.5/RT)$	Howard et al. (1973)
R6 $CO + OH = CO_2 + H$	$\ln k_6 = 10.847 + 3.995 \times 10^{-4} T$	Baulch et al.(1976)
R7 $CO + NO = 1/2 N_2 + CO_2$	$-r_{NO} = \frac{k_{iii} P_{NO} (k_{ii} P_{CO} + k_i)}{k_{iii} P_{NO} + k_{ii} P_{CO} + k_i}$ $k_i = 1.5 \times 10^{-3} \exp(-167.2/RT)$ [mol/cm ² /s] $k_{ii} = 7.33 \times 10^{-7} \exp(-79.4/RT)$ [mol/cm ² /s/kPa] $k_{iii} = 2.08 \times 10^{-4} \exp(-108.7/RT)$ [mol/cm ² /s/kPa]	Chan et al.(1983)
$k^* = A T^\alpha \exp(-E/RT)$		
	A [cm ³ , moles, s]	α E[kJ/mol]
R8 $NH + O_2 = NO + OH$	1.0×10^{10}	0 0
R9 $NH + O_2 = HNO + O$	1.0×10^{12}	0 13.59
R10 $NH + NO = N_2 + OH$	1.0×10^{13}	0 0
R11 $NH + OH = NO + H_2$	1.6×10^{12}	0.56 6.28
R12 $HNO + OH = NO + H_2O$	3.6×10^{13}	0 0
R13 $HNO + M = H + NO$	3.0×10^{16}	0 203.5
R14 $H + O_2 = OH + O$	2.24×10^{14}	0 70.3
R15 $O + H_2 = OH + H$	1.8×10^{10}	1 68.6
R16 $H_2 + OH = H_2O + H$	1.17×10^9	1.3 15.26
R17 $OH + OH = H_2O + O$	6.3×10^{12}	0 4.56
R18 $H_2 + M = H + H + M$	2.23×10^{12}	0.5 387.4
R19 $OH + H + M = H_2O + M$	2.2×10^{22}	-2 0
R20 $N + OH = NO + H$	4.1×10^{13}	0 0
R21 $N + O_2 = NO + O$	6.4×10^9	1 26.14
R22 $N + NO = N_2 + O$	1.55×10^{13}	0 0
R23 $N + O + M = NO + M$	6.44×10^{16}	-0.5 0
R24 $N + N + M = N_2 + M$	1.55×10^{17}	-0.837 0
R25 $O + O + M = O_2 + M$	1.9×10^{13}	0 -7.49

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

$$D_r \left(\frac{\partial^2 C_{O_2}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{O_2}}{\partial r} \right) = \frac{\xi \rho_B R_C}{M_C} \quad (1)$$

where

$$R_C = -\frac{dW_C}{d\theta} = (\eta A_g + A_r) k_1 P_{O_2} \quad (2)$$

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:

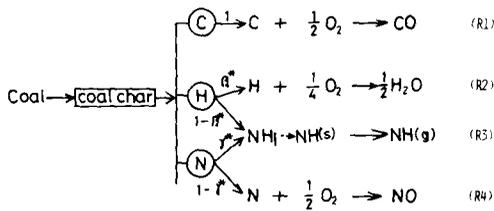


FIG. 1. Reaction mechanism of heterogeneous char combustion

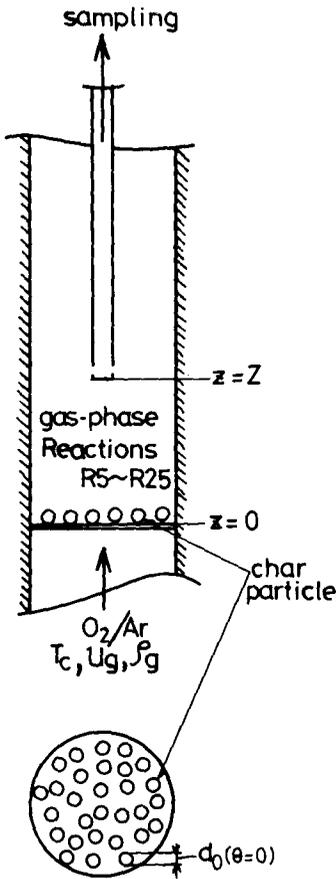


FIG. 2. Geometric configuration of the isothermal reaction system

$$C_{O_2} = 0 \quad \text{at } \theta = 0 \text{ for all } r \quad (3)$$

$$\frac{\partial C_{O_2}}{\partial r} = 0 \quad \text{for } \theta > 0 \text{ and } r = 0 \quad (4)$$

and

$$D_r \left(\frac{\partial C_{O_2}}{\partial r} \right) = h_D (C_{O_2, \infty} - C_{O_2}) \quad \text{at } r = r_0 \quad (5)$$

The effective diffusivity, D_e , can be estimated using the following relation derived from Bosanquet's equation¹²:

$$D_e = \epsilon_s^p \frac{1}{(1/D_{K-O_2}) + (1/D_{O_2-Ar})} \quad (6)$$

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 literature¹³. In the present work, the value of p is assumed to be 2.0. The effectiveness factor, η , in Eq. (2) can be also calculated from the existing theory¹⁴.

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

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (7)$$

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:

$$R_H (= -dW_H/d\theta) = (\beta^* W_H/W_C) R_C \quad (8)$$

$$R_N (= -dW_N/d\theta) = ((1-\gamma^*) W_N/W_C) R_C \quad (9)$$

$$R_{NH} (= -dW_{NH}/d\theta) = (\gamma^* W_N/W_C) R_C \quad (10)$$

Homogeneous gas-phase reaction

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

$$R_{i,1} + R_{i,2} + R_{i,3} \xrightleftharpoons[k_i^-]{k_i^+} P_{i,1} + P_{i,2} + Y_k \quad (i=1, 2, \dots, N) \quad (11)$$

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

$$\begin{aligned} & \frac{\partial C_{Y_k}}{\partial \theta} + u_g \frac{\partial C_{Y_k}}{\partial z} \\ & = \sum_{i=1}^N (k_i^+ C_{R_{i,1}} C_{R_{i,2}} C_{R_{i,3}} - k_i^- C_{P_{i,1}} C_{P_{i,2}} C_{Y_k}) \end{aligned} \quad (k=1, 2, \dots, m) \quad (12)$$

where C_{Y_k} is the concentration of Y_k [mol/cm³].

The equations of conservation for the species to be analyzed (Y_1, Y_2, \dots, Y_m) can be introduced similarly.

The initial conditions for $\theta = 0$ and all values of z are

$$C_{O_2} = C_{O_2,0}, \quad C_{Ar} = C_{Ar,0} \quad (13)$$

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

Using assumption (5), the boundary conditions for CO, NO, NH, H₂O, O₂ and Ar are:

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

$$C_{CO} = 1/RT_C(1+B/R_C) \quad (14)$$

$$C_{NO} = 1/RT_C[1+(B/R_N)(M_H/M_C)] \quad (15)$$

$$C_{NH} = 1/RT_C[1+(B/R_{NH})(M_{NH}/M_C)] \quad (16)$$

$$C_{H_2O} = 1/2RT_C[1+(B/R_H)(M_H/M_C)] \quad (17)$$

$$C_{O_2} = C_{O_2,0} - (C_{CO} + C_{NO} + C_{H_2O})/2 \quad (18)$$

and

$$C_{Ar} = P_T/RT_C - (C_{CO} + C_{NO} + C_{NH} + C_{H_2O} + C_{O_2}) \quad (19)$$

where

$$B = u_g \rho_g A_T (\eta A_g + A_e) (M_c / M_{av}) / 4\pi r_0^2 n \quad (20)$$

and

$$M_{av} = (RT_C/P_T)(M_{Ar}C_{Ar,0} + M_{O_2}C_{O_2,0}). \quad (21)$$

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

The boundary conditions for the other species are

$$C_{Y_k} = 0 \text{ for } \theta > 0 \text{ and } z = 0 \quad (22)$$

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, η_{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 N₂ at the temperatures of 1273, 1373 and 1473 K (T_{py}) 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, θ_D , of a single char particle with an initial diameter, d_0 , measured in an O₂-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 O₂/Ar mixture used as an oxidizer was preheated to a predetermined combustion temperature (T_e) 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 (O₂-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 O₂/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 NO₂, HCN and NH₃ 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_1 , 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

	C (wt %)	H (wt %)	N (wt %)	Fuel Ratio
Activated Sludge	22.17	4.28	4.60	4.16
char (1273K)	16.62	0.16	0.90	
" (1373K)	14.52	0.12	0.49	
" (1473K)	14.31	0.09	0.40	
Taiheiyō coal	67.86	5.71	1.35	1.13
char (1273K)	63.40	0.41	0.83	
" (1373K)	62.39	0.29	0.59	
" (1473K)	61.60	0.18	0.43	
Taisei coal	79.11	2.61	0.90	0.12
char (1273K)	75.60	0.43	0.65	
" (1373K)	74.99	0.35	0.63	
" (1473K)	74.09	0.34	0.59	

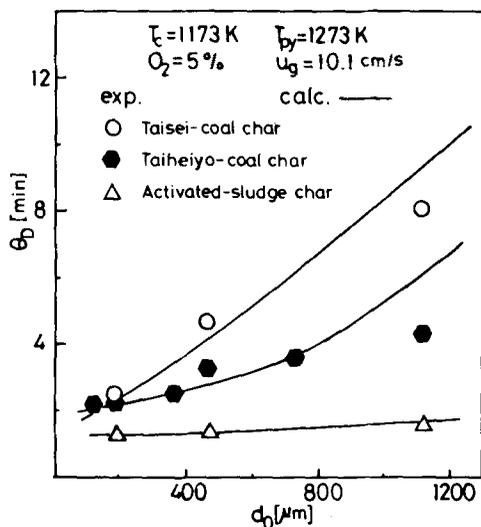


FIG. 3. Complete combustion-time of a single particle of coal char

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

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

parent coal	Taisei coal	Taiheiyō coal	Activated sludge
bulk density of			
particle ρ_p [g/cm ³]	1.25-1.4	0.68-0.8	0.65-0.75
porosity ϵ_s	0.15-0.23	0.35-0.55	0.62-0.7
specific internal surface area A_g [m ² /g]	5-10	15-20	60-110

3.2 Complete combustion time of a single particle of char

The calculated and the experimental results for the complete combustion time, θ_D , of a single particle of char compared confirm the validity of the theoretical model. The calculated values of θ_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 γ^*

Before determining γ^* 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 η_{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 $A_p = (\pi/4)nd_0^2$ and A_T is the cross-sectional area of the reaction tube. η_{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 $A_p/A_T <$

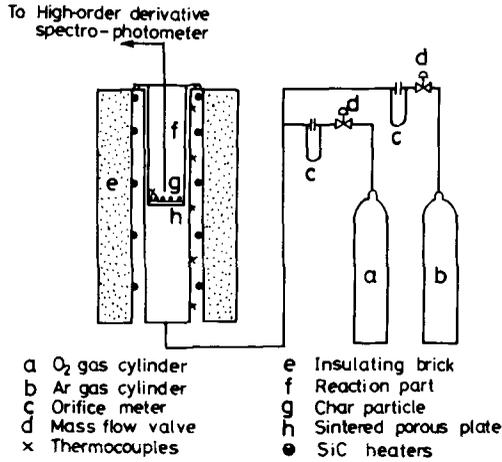


FIG. 4. Schematic diagram of experimental apparatus

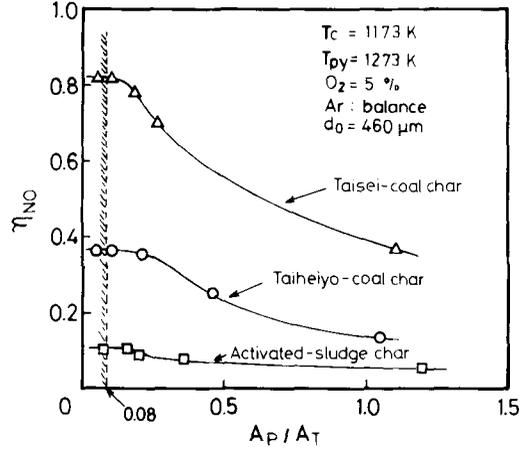


FIG. 6. Effect of apparent number of packed-particle-layers on the overall fractional conversion of char-N into char-NO

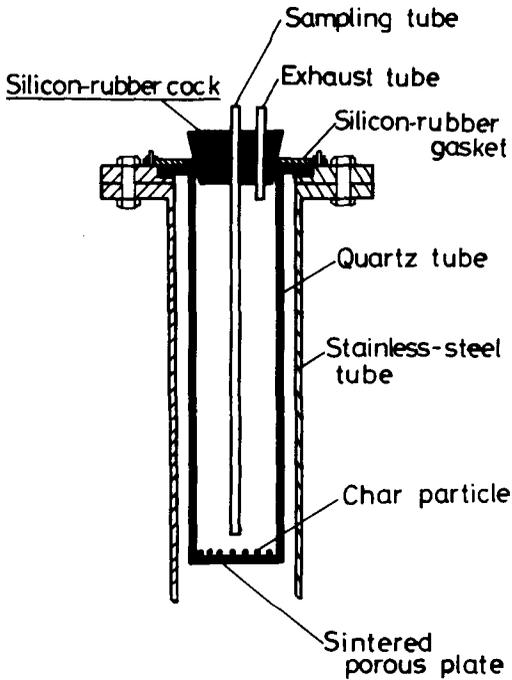


FIG. 5. Details of main reaction-vessel

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 γ as a parameter

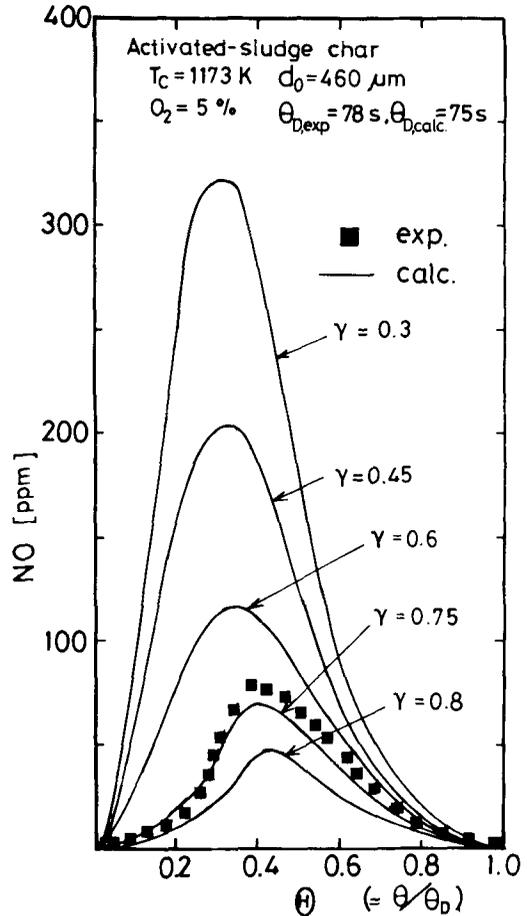


FIG. 7. Transient formation of char-NO during combustion of a single particle of char

i.e., γ^*). For increasing values of γ , the theoretical curve is expected to approach the experimental one, coinciding at a certain value of γ . To determine the proper value of γ^* 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 γ (Fig. 8). The values of γ^* can thus be determined graphically. The γ^* -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

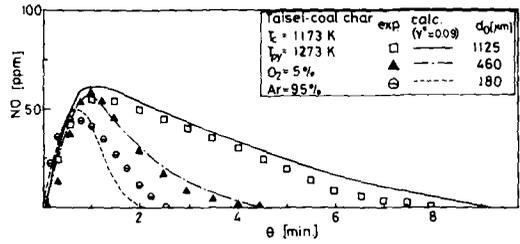


FIG. 10. Comparison of the calculated results with the experimental data for the transient formation of char-NO: Effect of the initial diameter of the char particle

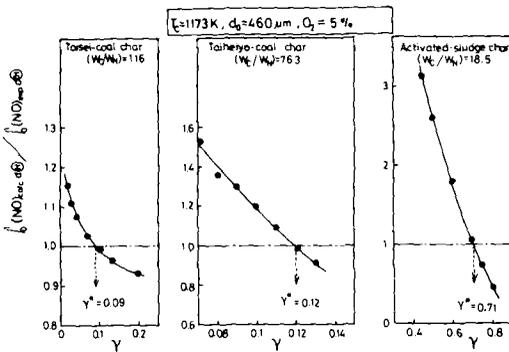


FIG. 8. Graphical determination of γ^*

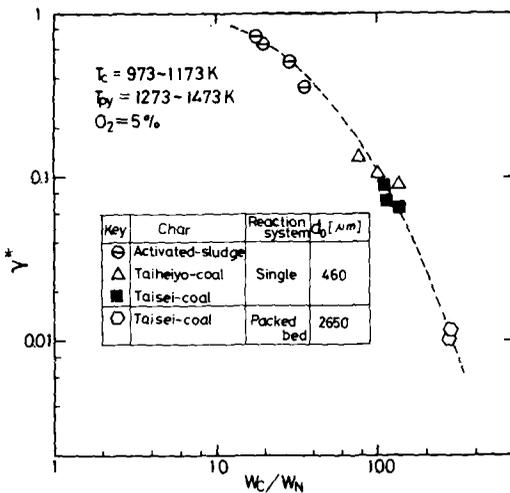


FIG. 9. Experimental relationship between γ^* and W_C/W_N

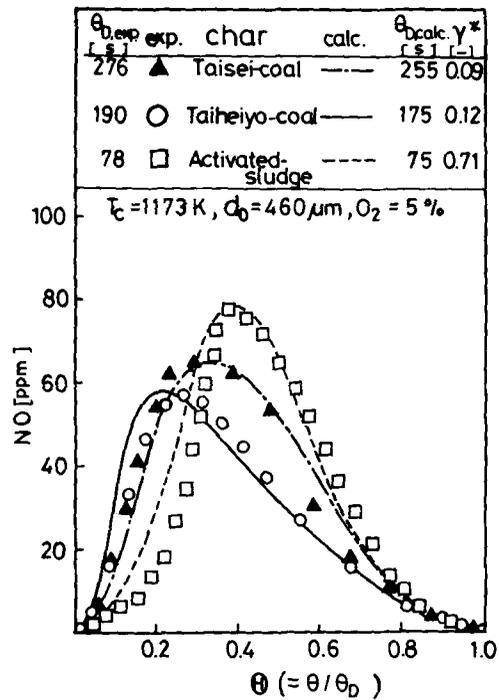


FIG. 11. Comparison of the calculated results with the experimental data for the transient formation of char-NO: Effect of the combustibility of the char particle

char-NO during the combustion of a single particle of char, with the value of γ^* 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, $T_{py} = 1273\text{--}1473$ K, $d_0 = 180\text{--}1125$ μm and $O_2 = 3\text{--}10$ 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 η_{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.

Key	E_a [K]	T_{py} [K]	Char	E_a [K]	T_{py} [K]	Char
Δ	1073	1273	Taisei-coal	\odot	973	1273
\blacktriangle	1173	1273		\odot	1073	1273
\blacktriangle	1073	1373		\odot	1173	1273
\blacktriangle	1173	1373		\square	973	1273
\blacktriangle	1073	1473		\square	1073	1273
\blacktriangle	1173	1473		\square	1173	1273
\circ	973	1273	Taiheiyo-coal	\square	973	1373
\circ	1073	1273		\square	1073	1373
\circ	1173	1273		\square	1173	1373
\circ	973	1373		\square	1173	1473
\circ	1073	1373		\square	1073	1473
\circ	1173	1373		\square	1173	1473

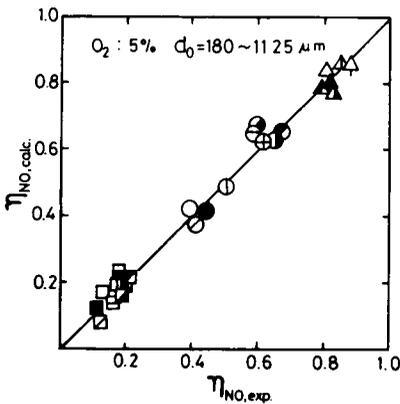


FIG. 12. Overall fractional conversion of char-N into char-NO over the entire period of combustion

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 = frequency factor
- A_e = specific external surface area of particle [cm²/g]
- A_g = specific internal surface area of particle [cm²/g]
- C_i = concentration of i -species [mol/cm³]
- $C_{O_2,\infty}$ = bulk concentration of oxygen [mol/cm³]
- D_e = effective diffusivity [cm²/s]
- D_{K-O_2} = Knudsen diffusivity [cm²/s]
- D_{O_2-Ar} = molecular diffusivity [cm²/s]
- d_0 = initial diameter of char particle [cm]
- E = energy of activation [kJ/mol]
- h_D = mass transfer coefficient [cm/s]
- k_1 = intrinsic rate constant on area basis for oxidation of char-C [g-C/cm²/s/kPa]
- k^+, k^- = forward and reverse rate constant, respectively, for a homogeneous gas-phase reaction
- M_i = molecular weight of i -species [g/mol]
- n = total number of char particles in the packed bed
- P_i = partial pressure of i -species [kPa]
- P_T = total pressure [kPa]
- R = universal gas constant [cm³·kPa/mol/K, kJ/mol/K]
- Re = Reynolds number for the particle
- R_j = overall rate of release of the j -component of the char [g/g/s]
- r = radial distance from the center of the particle [cm]
- Sc = Schmidt number
- Sh = Sherwood number
- T_c = combustion temperature [K]
- T_{py} = pyrolysis temperature [K]
- u_g = linear velocity of reactant gas [cm/s]
- W_j = mass concentration of j -component of the char [g/g]
- Z = distance from porous plate to point of gas sampling [cm]
- z = distance from porous plate [cm]
- Greek symbols*
- β^* = characteristic parameter of the proposed kinetic model
- γ = parameter of calculation

γ^*	= characteristic parameter of the proposed kinetic model
ϵ_s	= porosity of a particle of char
ζ	= stoichiometric coefficient for reaction R1
η	= effectiveness factor
η_{NO}	= overall fractional conversion of char-N into char-NO
Θ	= dimensionless reaction time (θ/θ_0)
θ	= reaction time [min,s]
θ_D	= complete combustion time of a single particle of char [min,s]
ρ_B	= bulk density of a particle of char [g/cm ³]
ρ_g	= density of reactant gas [g/cm ³]
<i>Subscript</i>	
0	= initial

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