Formation Mechanism of Thermal NO_x in Pulverized Coal Combustion*

Ken OKAZAKI**, Kazuo SUGIYAMA** and Isao YURI**

The effects of various basic factors of combustion conditions and coal properties on thermal NO_x formation behaviors in pulverized coal combustion have been experimentally clarified, and a theoretical analysis for the flame structural change around a coal particle has been performed, including full chemical kinetics of prompt NO_x formation. Thermal NO_x concentrations much higher than those predicted by the extended Zeldovich mechanism have been experimentally observed even in the usual pulverized coal combustion conditions. The contribution of thermal NO_x to the total NO_x rapidly increases with the increase of flame temperature and oxygen-fuel stoichiometric ratio, especially for highly volatile coals. Both the large amount of thermal NO_x formation and the effects of various factors on it have been well explained by considering the prompt NO_x formation in the flame zone around each coal particle through HCN and NH formed by the reactions between N_2 in air and hydrocarbons in the evoluted volatile matter.

Key Words: Combustion, Solid Fuel, Combustion Products, Furnace, Chemical Reaction, Fossil-Fuel-Fired Power Generation, Pulverized Coal Combustion, NO_x Formation, Thermal NO_x

1. Introduction

Nitric oxides (NO_x) can be formed, in general, from oxidation of nitrogen compounds in the fuel (fuel NO_x) and the fixation of atmospheric nitrogen (thermal NO_x), but fuel NO_x is considered to be the major contribution to the total NO_x for the usual burning conditions of pulverized coal[1),2)]. This is the reason why most of the recent studies on NO_x in pulverized coal combustion[3)-10)] have been devoted to identifying the mechanism of conversion processs from coal-N (volatile-N and char-N) to NO_x and why most theoretical studies[11),12)] have neglected the formation of thermal NO_x. These continuing energetic studies have revealed the important features of NO_x formation and the method of suppressing it by staging or controlling the local burning conditions in the furnance. Actually, the technologies to simultaneously reduce in-furnance NO_x concentration to less than 150 ppm and unburnt carbon in ashes to less than 5 wt% have already been achieved in Japan[13)].

Such progress in low-NO_x combustion technology has changed the situation, resulting in the increase of the relative importance of thermal NO_x contribution even in pulverized coal combustion. However, thermal NO_x formation behavior in pulverized coal combustion and its mechanisms have not been investigated in detail.

The purpose of this study is to clarify the fundamental and general features of thermal NO_x formation characteristics in pulverized coal combustion through experiments and theoretical analyses. First, the pure effects of various important factors of the oxygen-fuel stoichiometric ratio, initial oxygen concentration, maximum flame temperature, and coal properties of volatile matter and nitrogen content are experimentally investigated. Then, the mechanisms of these effects are clarified by theoretical analyses which include full chemical kinetics of prompt NO_x formation in the flame zone around each coal particle. Although the term "prompt NO_x" is generally used for the NO_x rapidly formed in the premixed fuel-rich hydrocarbon flame[14)], here we use it for the NO_x formed in the flame zone around coal particles through the intermediate species of HCN and NH_i from the reactions of N_2 in air with hydrocarbons evoluted from coal particles as volatile matter.

2. Experimental System and Procedure

The one-dimensional combustion furnance used in the experiments and its flow system are almost the same as our previous one[9),15)] but it has been recon-

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** Department of Energy Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441, Japan

structed so as to suit our present study. The furnance is 1.5 m in length, 8 cm in inner diameter and constructed with water-cooled steel cylinders with heat-insulating refractory coated on the inside. Moreover, argon gas lines have been newly attached to supply a nitrogen-free Ar/O_2 mixture. An air preheating system and O_2 injector have also been installed to independently control the flame temperature and initial oxygen concentration. The gaseous samples were analyzed by using standard continuous instruments of chemiluminescent NO_x, paramagnetic O_2, NDIR CO/CO_2 and FID total hydrocarbon to monitor the combustion.

Ultimate and proximate analyses of the three kinds of coals, A, B and C, used in this study are shown in Table 1. Coals A and B are lignite and subbituminous and have almost the same volatile matter content (VM) but much different nitrogen content (N). On the other hand, bituminous coal C has much lower volatile matter content than those of A and B but almost the same high content of fuel nitrogen as that of coal B.

Experiments are performed for widely varied experimental parameters of the oxygen-fuel stoichiometric ratio λ(0.8-1.4), initial oxygen concentration R_{O_2}(21−27 vol%) and maximum flame temperature T_{max}(1 100-1 600°C). In order to derive the pure effects of these various experimental parameters, CR values, defined as the ratio of measured NO_x concentration to that of 100% conversion from fuel-N under the same given experimental condition, are mostly used in the data reductions not only for fuel NO_x but also for thermal NO_x and total-NO_x in this study. According to the fact that interactions between fuel NO_x and thermal NO_x are not of first-order importance[1], thermal NO_x can be specified by subtracting fuel NO_x obtained by use of $Ar+O_2$ as an oxidant from total NO_x by N_2+O_2 at a given condition with the relevant basic factors being perfectly matched.

3. Experimental Results and Discussion

The concentration profiles of total NO_x and fuel NO_x have their maximum values near the position of maximum flame temperature and then decrease gradually. Therefore, T_{max} was selected as one of the basic combustion parameters affecting NO_x formation. In the following, the final NO_x concentrations measured at the exit of the furnance are used to discuss the NO_x formation characteristics.

Table 1 Coal properties

Coal	Proximate Analysis(%,dry) VM	FC	Ash	Ultimate Analysis(%,dry) C	H	O	N	S
A	44.4	39.8	15.8	65.4	5.47	12.5	0.79	0.21
B	40.8	49.2	10.0	71.4	5.3	10.9	1.50	0.74
C	26.1	58.7	15.2	70.5	3.64	8.3	1.64	0.99

VM : Volatile Matter, FC : Fixed Carbon

3.1 Effect of flame temperature

Temperature dependence of the formation characteristics of thermal NO_x and fuel NO_x for highly volatile coal A and its changes with the increase of oxygen-fuel stoichiometric ratio λ are shown in Fig. 1, where masured NO_x concentrations are converted to CR values defined above. On the whole, the CR values for total NO_x increase with the increase of maximum flame temperature T_{max} due to the increase of thermal NO_x formation, while the fuel NO_x is insensitive to the flame temperature. A temperature dependence of fuel NO_x, which might be evident for very high temperatures[1),3)], has not been observed in the temperature range tested in this study. For the temperatures below 1 200°C, thermal NO_x contributions in the total NO_x disappear. It is interesting that the CR values for total NO_x and fuel NO_x are almost on the same line, respectively, in spite of the different initial oxygen concentrations. This is consistent with our previous report[15] that oxygen concentration itself has little effect on NO_x formation if the maximum flame temperature is fixed. Although a higher oxygen concentration elevates the particle temperature and promotes the evolution of volatile matter, its effect may have been compensated by the contraction of the flame zone around coal particles where prompt NO_x is mainly formed, as will be discussed in the theoretical analysis.

It is also shown in Fig. 1 that the temperature dependency of thermal NO_x increases with the increase of the oxygen-fuel stoichiometric ratio λ. For the flame temperature of 1400°C, the contribution of thermal NO_x to the total NO_x is 15% for $\lambda=0.8$ and 1.0, 22% for $\lambda=1.2$, and 33% for $\lambda=1.4$. Although the result for $\lambda=1.2$ is almost the same as that of Pershing and Wendt[1], much larger amounts of thermal NO_x are formed for larger values of λ if the temperature is fixed.

The results shown in Fig. 1 should change depending on the coal properties. Figure 2 shows such effects with the oxygen-fuel stoichiometric ratio fixed at 1.2. Temperature dependence of thermal NO_x decreases with the decrease of volatile matter in coal. At the temperature of 1 400°C, while the contribution of thermal NO_x to the total NO_x is 22% for highly volatile coals A and B, it decreases to 15% for low-volatility coal C. In the latter case, the CR values for both thermal NO_x(CR_{th}) and fuel NO_x(CR_f) are much lower than those for coals A and B. The large values of both CR_{th} and CR_f for coal A are due to the low nitrogen content of coal A[15].

3. 2 Effect of oxygen-fuel stoichiometric ratio

From raw data such as those shown in Fig. 1, the pure effects of the oxygen-fuel stoichiometric ratio λ can be derived by determining the CR values for various fixed values of flame temperature. The results thus obtained for coals A, B and C are shown in Fig. 3 for the maximum flame temperatures of 1 300, 1 400 and 1 500°C. As for the thermal NO_x, not only the values of CR_{th} but also the concentrations of thermal NO_x reduced to those at the standard condition of R_{O_2} =21 vol% and λ=1.0 are also shown in the lower figures.

It is shown that the dependence of thermal NO_x on the oxygen-fuel stoichiometric ratio λ is much larger than that of fuel NO_x, although both thermal NO_x and fuel NO_x increase with increase of λ. Thermal NO_x monotonously increases with λ, while fuel NO_x shows a tendency to saturate[16] for λ>1.2. Moreover, the increase of thermal NO_x with λ is much more significant for higher temperatures. In the case of a high temperature of 1 500°C for coal A, 33% and 42% of the total NO_x are due to thermal NO_x for λ= 1.2 and 1.4, respectively. On the other hand, only a small contribution of thermal NO_x can be observed for the case of the low temperature of 1 300°C, where only 10% of the total NO_x is due to thermal NO_x even for the fuel-lean condition of λ=1.2.

Figures 1, 2 and 3 show the strong effect of flame temperature in increasing the thermal NO_x formation.

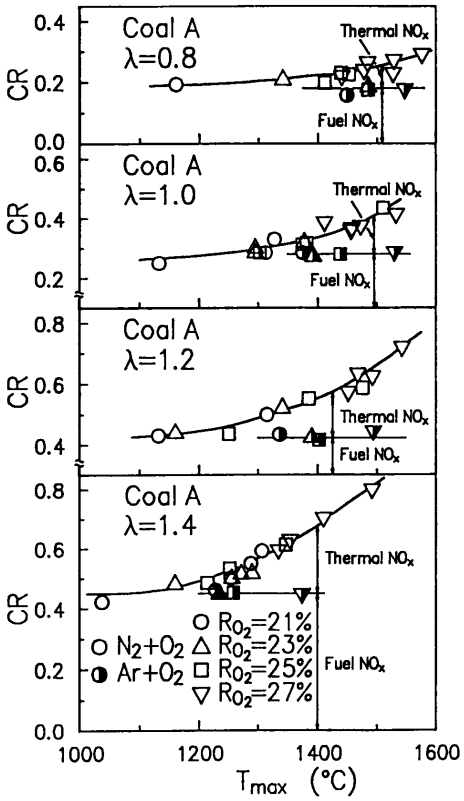

Fig. 1 Temperature dependence of thermal NO_x formation characteristics for coal A and its changes with oxygen-fuel stoichiometric ratio

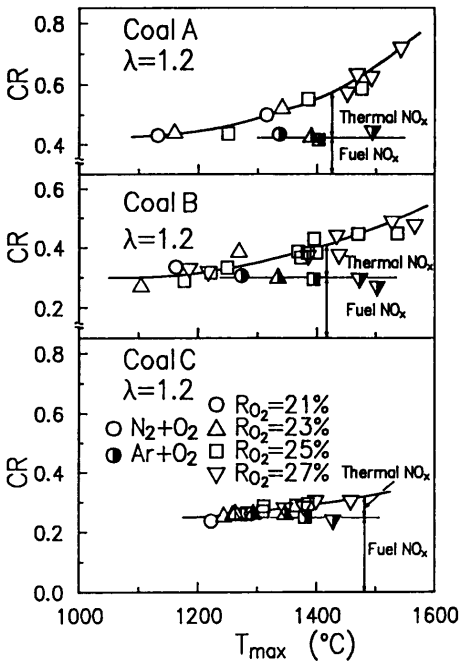

Fig. 2 Temperature dependence of thermal NO_x formation characteristics for a fixed oxygen-fuel stoichiometric ratio of 1.2 and its changes by coal types

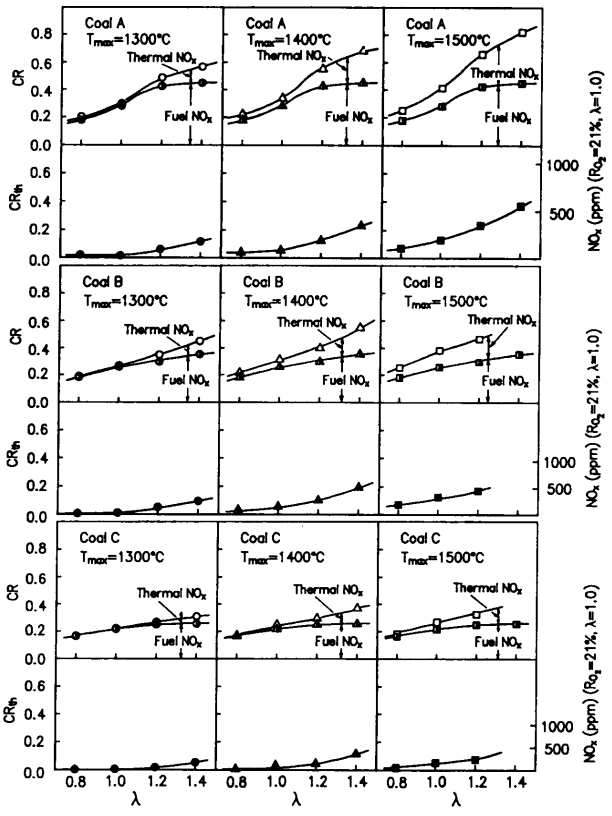

Fig. 3 Effect of oxygen-fuel stoichiometric ratio on thermal NO_x and fuel NO_x formation characteristics. The maximum flame temperatures are fixed at 1 300, 1 400 and 1 500°C

Here, the concentrations of Zeldovich NO_x formed by the well-known extended Zeldovich mechanism (Eqs. (10), (11) and (12) in section 4.2) were estimated. Because the volatile matter burns in a very short time and the Zeldovich NO_x is mainly formed in the post-flame, the increasing behavior of Zeldovich NO_x concentration was calculated with the oxygen concentration after the volatile matter combustion as the initial condition. The results obtained for the case of $\lambda=1.2$ and coal A are shown in Fig. 4. The broken line shows the residence time corresponding to the actual experiments.

According to this estimation, the Zeldovich NO_x concentration is only 1 ppm at the fixed temperature (T) of 1 800 K and 40 ppm at $T=2\,000$ K, and is much smaller than the thermal NO_x concentrations shown in Fig. 3. The large discrepancy cannot be explained even if we consider the fact that the actual particle temperature can be much higher than the flame temperature[17),(18)], especially in the region of volatile matter combustion.

In this paper, the prompt NO_x formed in the flame zone around coal particles during volatile matter combustion is considered to be the major source of the thermal NO_x, as shown in the theoretical analysis below. In pulverized coal combustion, the increase of temperature will expand for flame zone further away from the surface of coal particles, which results in the increase of prompt NO_x formation in it, while the prompt NO_x formation itself is usually affected very little by the temperature.

3.3 Effect of coal properties

Comparing the results for coals B and C having almost the same nitrogen content, the separate effect of volatile matter content on the thermal NO_x formation was derived. Larger values of volatile matter content result in the increase of thermal NO_x, and this effect is larger for higher values of T_{max} and λ. This effect can be explained as that the higher volatile matter content will result in the greater expansion of the hot flame zone around burning particles[17),(19),(20)], where the prompt NO_x can easily be formed[10)].

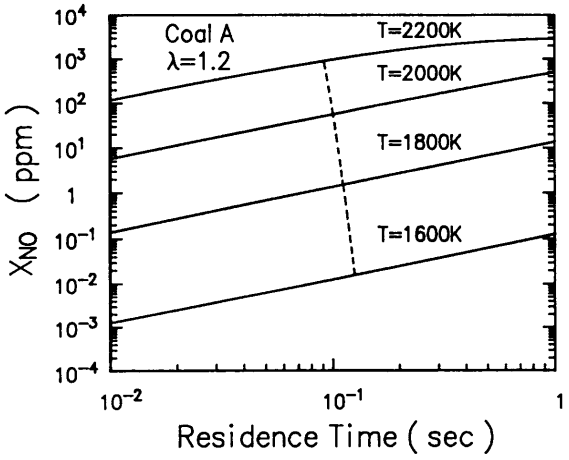

Fig. 4 Estimation of thermal NO_x formation only by the extended Zeldovich mechanism for coal A and oxygen-fuel stoichiometric ratio of 1.2

The separate effect of nitrogen content on the thermal NO_x formation can be derived by comparing the results for coals A and B having almost the same high volatile matter content. As a result, the effect of fuel nitrogen content on the thermal NO_x formation is quite small, and no significant effect has been observed.

4. Theoretical Analysis of Thermal NO_x Formation

Combining the full chemical kinetics scheme for laminar diffusion flames of methane[21)] with our model for the time-dependent changes of flame structure around a coal particle[17)], thermal NO_x formation behavior around a coal particle was theoretically analyzed. The purpose of this analysis is to show how a large amount of prompt NO_x can be formed near the particles, and is not to establish a strict model for predicting NO_x concentrations nor to discuss detailed chemical kinetics. Hence, the most simplified model fitting the present purpose is adopted in this study.

4.1 Analytical model

The following assumptions are introduced in the analysis.

(1) A coal particle is spherical and all phenomena considered are spherically symmetric.

(2) Only methane (CH_4) is considered as evoluted volatile matter.

(3) Fixed carbon is oxidized on the particle surface by O_2 and CO_2.

(4) Particle diameter is constant during the volatile matter combustion.

(5) Radial velocity is calculated from the evoluting flux of volatile matter and combustion products; then the momentum conservation equation is excluded.

(6) Gas and particle temperatures are the same and constant at the given value; then the energy conservation equation is excluded.

Based on the above assumptions, the fundamental equations consist of conservation equations of mass and species in the gas phase and mass of the solid phase. As for boundary conditions for the species concentrations, their gradients at the outer radius of the equivalent sphere occupied by one coal particle are given as zero. Raw coal and surrounding air are simultaneously set at the given temperature at the time $t=0$. Then, time-dependent changes of chemical structures in the flame around the particle are calculated.

4.2 Gas phase reaction model

Fuel NO_x is not considered in this model and only thermal NO_x formation behaviors are analyzed. In the analysis here, NO_x is treated as NO. The following 12 reactions are considered as those concerning nitrogen.

$$CH_2+N_2=HCN+NH \quad (1)$$
$$HCN+OH=CN+H_2O \quad (2)$$
$$CN+O_2=CO+NO \quad (3)$$
$$CN+O=CO+N \quad (4)$$
$$NH+OH=N+H_2O \quad (5)$$
$$NH+N=N_2+H \quad (6)$$
$$NH+NH=N_2+H_2 \quad (7)$$
$$N_2+OH=NO+NH \quad (8)$$
$$N_2+CO=NO+CN \quad (9)$$
$$N+OH=NO+H \quad (10)$$
$$N+O_2=NO+O \quad (11)$$
$$O+N_2=NO+N \quad (12)$$

The fragment of CH_4 reacts with N_2 in air to produce HCN and NH (reaction (1)), which then react with OH to yield CN and N (reactions (2) and (5)). Through the oxidation of those intermediate species, the prompt NO is formed in the flame zone around a coal particle. Reactions (10), (11) and (12) correspond to the extended Zeldovich mechanism and form Zeldovich NO. Numerical calculations have been performed considering 20 chemical species and 44 elemental reactions, whose kinetics data were evaluated by citing the references[21),22]. Zeldovich NO can be separately specified by stopping reaction (1).

4.3 Analytical results and discussion

Figures 5 and 6 show the time-dependent concentration profiles of chemical species around a particle of coal A with a diameter of 70 μm immersed in the constant temperature field of 1 700 K and $R_{O_2}=21$ vol%. HC in Fig. 5 is the sum of CH_4, CH_3 and CH_2. In the stage of volatile matter combustion, the flame zone, whose position is defined as that of the intersection of HC and O_2, is pushed away from the particle surface in a very short time by the evolution of volatile matter and then shrinks back to the particle surface with the consumption of volatile matter. The times shown in these figures are rather short because the preheating time is not taken into account. It is shown in Fig. 6 that large amounts of HCN and NH are actually formed in the fuel-rich zone inside the flame, resulting in NO formation slightly outside the flame. The NO formed in the flame zone will diffuse to the outer region with the progress of time.

Comparison between thermal NO and Zeldovich NO concentration profiles around a particle at the time $t=5$ ms is shown in Fig. 7. Zeldovich NO gives only a small contribution to the thermal NO, and the rest is due to the prompt NO. Here, it has been clarified for the first time that the thermal NO formation in pulverized coal combustion is mostly due to the prompt NO formed in the flame zone around coal particles.

The NO concentration profiles thus obtained at each time have been averaged in space, and the changes of thermal NO and Zeldovich NO concentrations with elapsed time have been obtained as shown in Fig. 8, including the effect of temperature. Average concentrations of thermal NO rapidly increase in the stage of volatile matter combustion and subsequently saturate. These results are quite reasonable because the thermal NO is mainly due to the prompt NO formed in the flame zone around coal particles during the volatile matter combustion. Now, the large discrepancy between the measured thermal NO_x concentration and that of estimated Zeldovich NO_x, as mentioned in the previous section 3.2, has been very well explained by considering the prompt NO_x formation. Although the actual combustion behavior of coal particles in pulverized coal combustion[20),23] is not so

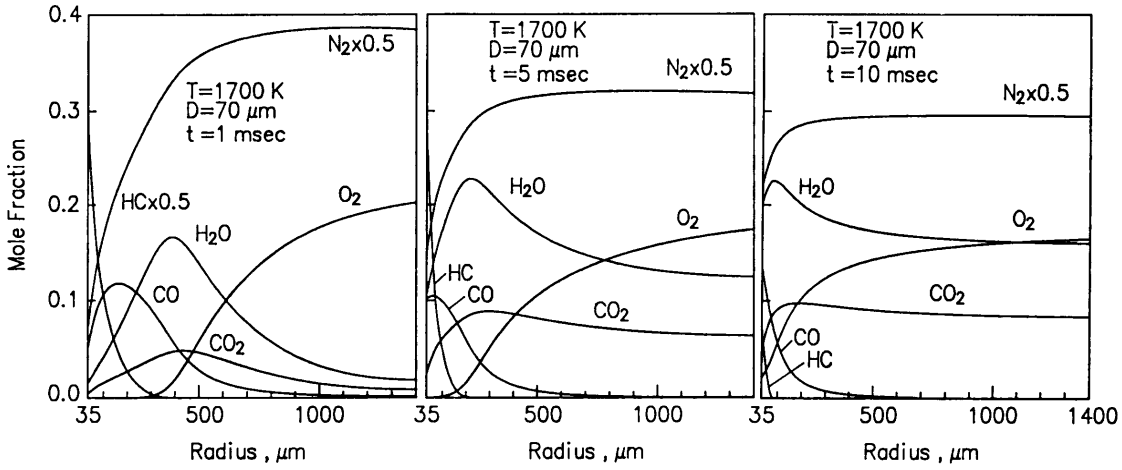

Fig. 5 Time-dependent concentration profiles of major stable chemical species in the flame around a coal A particle of 70 μm in diameter at the temperature of 1 700 K

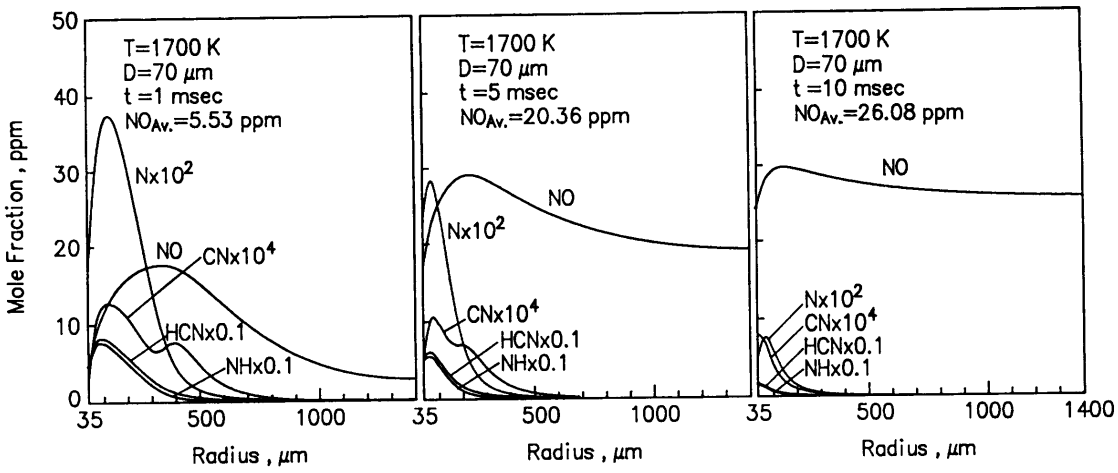

Fig. 6 Time-dependent concentration profiles of nitrogen-containing chemical species in the flame around a coal A particle of 70 μm in diameter at the temperature of 1 700 K

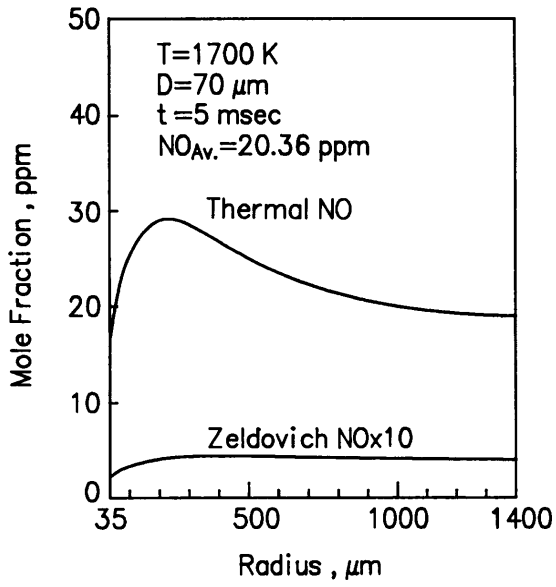

Fig. 7 Comparison of the concentrations and their profiles of thermal NO and Zeldovich NO around a coal A particle of 70 μm in diameter at $T=1\,700$ K and $t=5$ ms

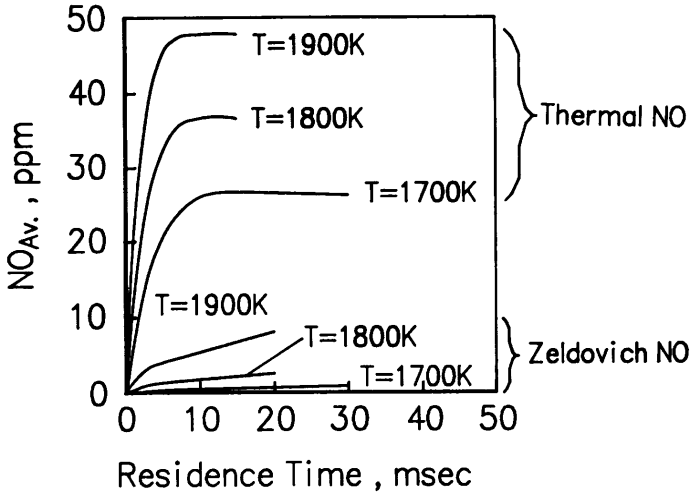

Fig. 8 Increasing behavior of average concentrations of thermal NO and Zeldovich NO with elapsed time and the dependencies on temperature for a 70-μm particle of coal A

simple as the model adopted in this analysis, it should be true that the thermal NO_x is mainly due to the prompt NO_x.

The very slight effect of initial oxygen concentration (R_{O_2}) on the thermal NO_x formation, as discussed in the experiments, can also be well explained by this analysis which includes prompt NO_x formation, as shown in Fig. 9. The radius of the flame center at $t=$ 1 ms decreased from 310 μm for $R_{O_2}=21$ vol% to 260 μm for $R_{O_2}=27$ vol%, and this shrinkage of the flame zone cancelled the pure effect of oxygen concentration on the thermal NO_x formation.

5. Conclusions

Thermal NO_x formation characteristics in pulverized coal combustion have been investigated both experimentally and theoretically, and the following conclusions have been derived.

1) A much larger amount of thermal NO_x can be formed than that predicted by the extended Zeldovich mechanism for the maximum flame temperature. This is mainly due to the prompt NO_x formation in the flame zone around coal particles during volatile matter combustion.

2) Thermal NO_x contribution to the total NO_x rapidly increases with the increase of maximum flame temperature, and this tendency is much stronger for higher values of oxygen-fuel stoichiometric ratio and volatile matter content.

3) Initial oxygen cncentration does not have such a significant effect on the thermal NO_x formation under the same maximum flame temperature. This is due to the fact that the shrinkage of the expanding

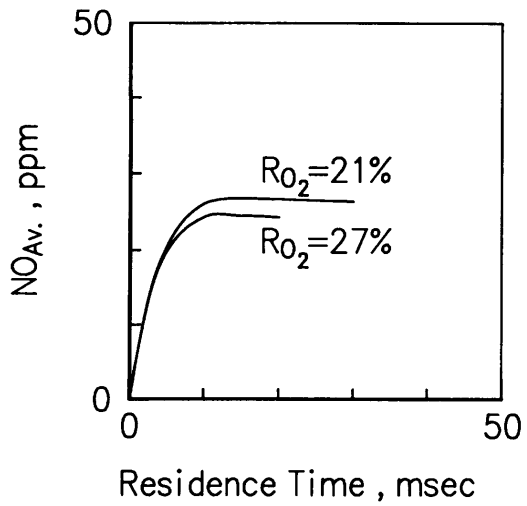

Fig. 9 Effect of initial oxygen concentration in the oxidant on the formation behavior of thermal NO for a 70-μm particle of coal A

flame zone around coal particles negates the pure effect of the increase of oxygen concentration.

4) Thermal NO_x formation monotonously increases with the increase of the oxygen-fuel stoichiometric ratio, while the fuel NO_x formation tends to saturate at an oxygen-fuel stoichiometric ratio larger than 1.2. The former tendency is more significant for higher flame temperature and higher volatile matter content.

5) Coals of higher volatile matter content result in the increase of thermal NO_x formation especially for the case of high temperature and large oxygen-fuel stoichiometric ratio. This is due to the expansion of the flame zone around coal particles where the prompt NO_x is easily formed.

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