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NO_x emission from high-temperature air/methane counterflow diffusion flame [☆]

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Abstract

The objectives of the present study are to measure NO_x emission of counterflow diffusion flame, to compare the findings with numerical results, and finally to demonstrate efficacious effect of high-temperature air with low concentration of oxygen on NO_x emission. Recently, high-temperature air with low concentration of oxygen is used for various industrial furnaces, resulting high efficiency and low emission of pollutants. Since high-temperature air increases NO_x emission and air with low concentration of oxygen decreases it, these effects are competitive. Measurement and computation were conducted to clarify these two effects by use of counterflow diffusion flame. Since it is difficult to employ very high temperature over 1100 K in a laboratory-scale apparatus, a quantitative agreement between experimental and numerical results was confirmed first, and then a numerical approach was used to obtain a larger effect of low oxygen to reduce NO_x emission. In the experiments, the methane concentration is changed from 10 to 30 vol% diluted by nitrogen, oxygen from 10 to 21 vol%, and air temperature from room temperature to 1100 K. The total amount of NO_x sufficiently agreed between experimental and numerical results, although NO and NO_2 could not be separated. By the numerical method, it was found that NO_x emission from the counterflow diffusion flame of high-temperature low-oxygen air of 1500 K and 5% oxygen is comparable with that of room-temperature air of 21% oxygen.

Keywords: NO_x emission; High-temperature air combustion; Counterflow diffusion flame; Low oxygen concentration

1. Introduction

A high-temperature air combustion system has recently been applied to industrial furnaces [1,2], because combustion of this system is very stable and therefore the oxygen concentration in air can be decreased as low as 3%. As a result, NO_x emission can be significantly reduced [1,3]. High-temperature air is produced by a regenerative heat exchanger, that is, the heat exchange media is heated by hot flue gas passing through it and then the airflow supplied from the opposite side is heated by the heat released from it. Combustion is strengthen by the preheated air and so it is very stable. The original concept is based on excess enthalpy flame.

Although low NO_x emission has been achieved by use of high-temperature air with low concentration of oxygen, the fundamental flame structure and the mechanism of low NO_x emission remain unclear. NO_x reduction may not be due only to the low concentration of oxygen: namely, a contributing factor may be high speed airflow supplementing the low concentration of oxygen and thereby enhancing strong turbulence [4]. In this paper, the two fundamental competitive effects of high-temperature and low-oxygen concentration are compared by use of counterflow diffusion flame, which is the most controllable over the convective environment and is very convenient for observing the phenomena and measuring NO_x emission.

Previous comparisons of experimental measurements with computational results for NO_x emission of counterflow methane flame [5] and CO/H_2 flame [6] have been reported. Although the spatial resolution in both of the cited experiments was not sufficient and the maximum value of measured NO_x around the flame was not consistent with

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the calculated one, qualitative agreement could be given and the fundamental aspect could be grasped. Computations on NO_x emission from counterflow diffusion flame by use of detailed chemistry based on the Miller and Bowman mechanism [7] have been made by Nishioka et al. [8], Ju [9] and Zhu et al. [10], indicating a decrease of the NO_x emission index [11] with the stretch rate. It is suggested that the decrease of NO_x emission with the increase of stretch rate may be due to the reduction of residence time in the high temperature region. On the other hand, the radiation heat loss plays an important role at very low stretch rates and the flame temperature decreases drastically near the extinction limit on the side of low stretch rates [12] as well as on the side of high stretch rate. Therefore, NO_x emission should have a maximum at a certain stretch rate.

In this paper, the effect of the air temperature and oxygen concentration on NO_x emission is investigated by using counterflow diffusion flame. First, measurement results of NO_x are compared with numerical results based on the GRI mechanism, showing a sufficient quantitative agreement. Second, by use of the numerical approach, it is indicated that the effect of low-oxygen concentration of air is strong and as a result NO_x emission can be reduced even if high-temperature air is used.

2. Experimental apparatus and methods

Fig. 1 shows the experimental setup of the counterflow diffusion flame. The exit diameter of the nozzle burners is 20 mm and the nozzle spacing is 14.9 mm. Airflow comes from the bottom burner through an air heater, in which hot combustion gas of a propane burner is passed through a porous heat regenerator on one side and fresh air is subsequently introduced from the opposite side and passed through the hot regenerator. The fresh air is heated and the regenerator is cooled such that one regenerator is always heated by switching the direction of flow [1, 2]. The air temperature can be raised to about 1200 K. Methane diluted by nitrogen is used as a fuel and is issued from the upper nozzle, and also nitrogen gas flow flows out from the outer nozzle in a concentric configuration to extinguish a flame overflowing needlessly. Since combustion gas heats the upper nozzle, it is cooled by a water jacket. All experiments were conducted at room temperature and one atmospheric pressure.

The flow rate of methane, air and nitrogen for dilution was adjusted by mass flow controllers. The stretch rate of the counterflow field was calculated by equation [13]:

$$\varepsilon = \left(V_{\mathrm{O}} + V_{\mathrm{F}}\sqrt{\rho_{\mathrm{F}}/\rho_{\mathrm{O}}}\right)/L$$

where ε denotes the stretch rate, V denotes nozzle exit velocity, ρ denotes density and L denotes nozzle spacing, and suffix O and F represent oxygen and fuel. All concentrations are expressed by the volume fraction.

The sampling system of NO_x is schematically shown in Fig. 2. The sampling glass probe with an exit height of 0.1 mm and a width of 0.8 mm was water-cooled to freeze reactions after sampling. The sampling was conducted perpendicularly along a line 2 mm apart from the centerline of the burner. Since the diffusion flame is established flatwise, the points on the line apart from the centerline has a radial flow velocity and are better for sampling than the centerline itself. The sampling gas is fed into a NO_x/O_2 analyzer

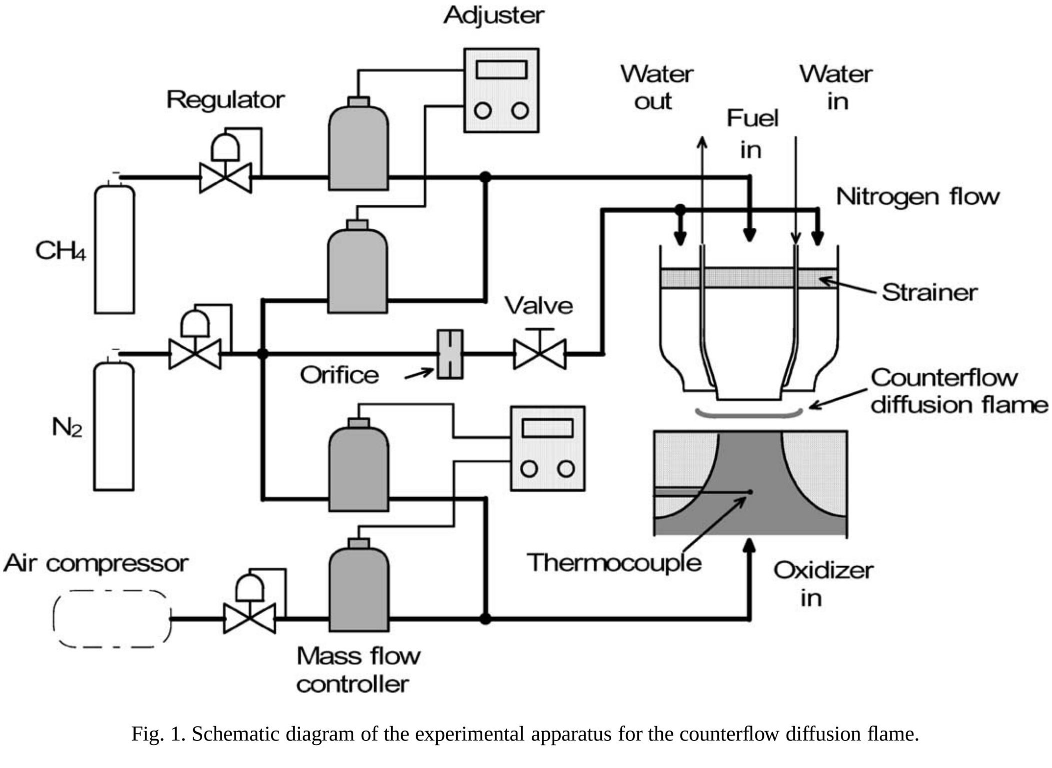


Fig. 1. Schematic diagram of the experimental apparatus for the counterflow diffusion flame.

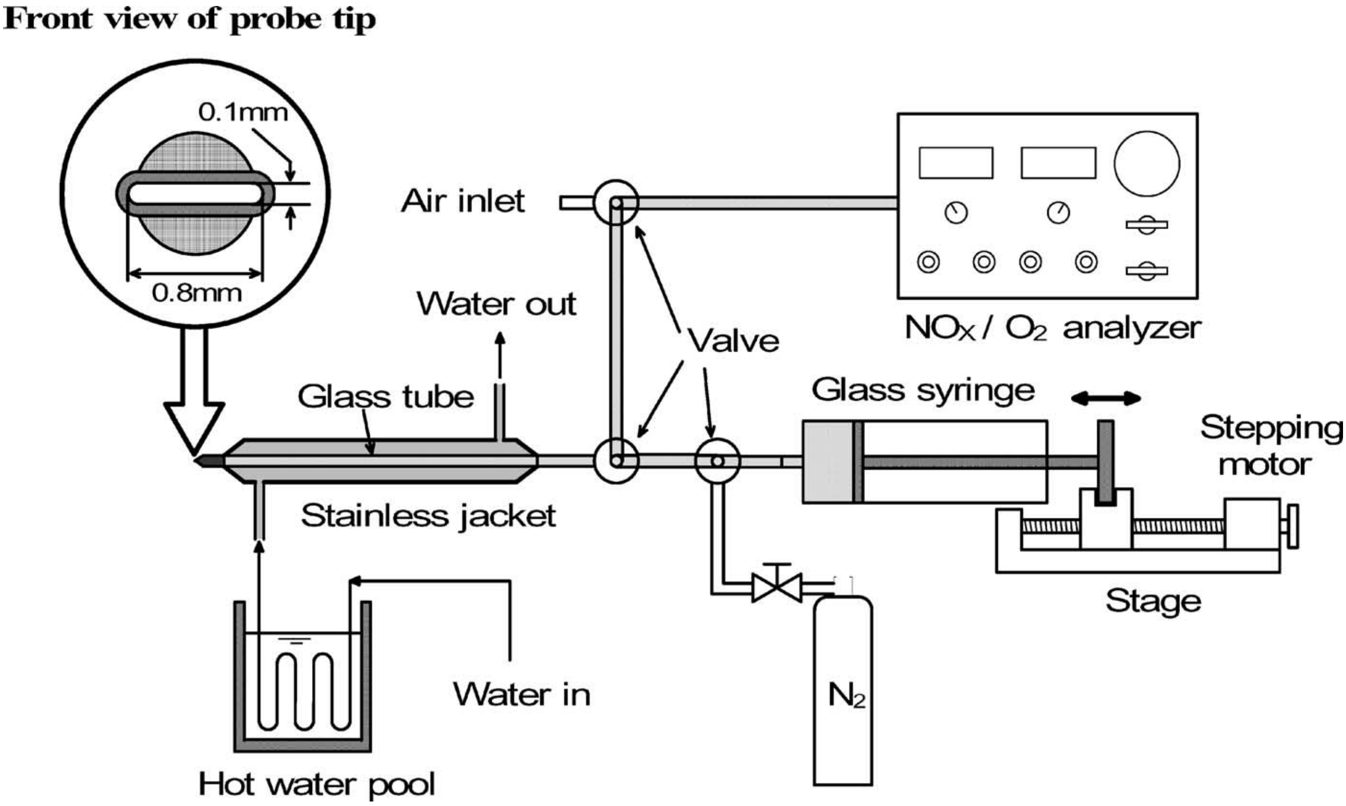


Fig. 2. Schematic of the sampling system of NO_x.

(Best Measuring Instruments, BCL-611 AS) by switching the flow channel after sampling. This instrument analyzes NO concentration as well as O_2 by the chemical luminescence method and the magnetic method, respectively, and can also measure NO_x $(= NO + NO_2)$ concentration by use of a NO_2–NO converter. Therefore, NO_2 concentration is obtained by subtracting the NO concentration from the NO_x concentration.

3. Numerical method

For comparison with experimental results, numerical simulation is performed by using the computer program of Ju [14] for a one-dimensional counterflow diffusion flame, which is a modification of PREMIX by Kee et al. [15]. Transport coefficients and thermodynamic properties were obtained from CHEMKIN II, and 48 chemical species and 277 elementary reaction steps were used to calculate NO_x reactions including prompt and thermal mechanisms, based on GRI scheme.

4. Results and discussion

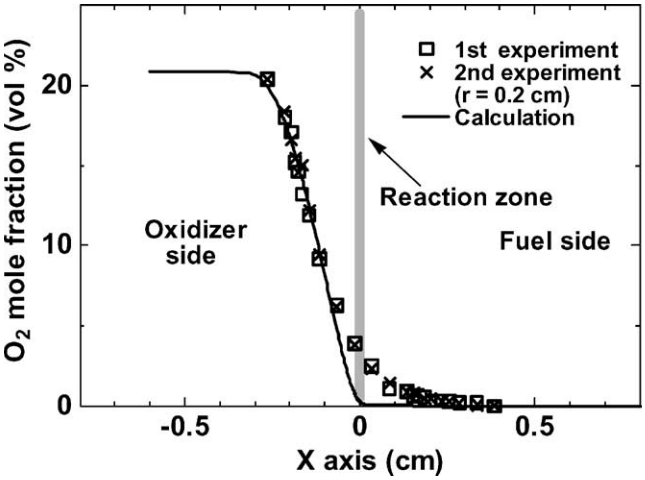


Fig. 3. Measured and calculated oxygen concentration profile along the centerline (21% O_2, 30% CH_4, $T_0 = 294$ K, $\varepsilon = 50$ sec^{-1}).

Fig. 3 presents a comparison of two experimental results of the O_2 mole fraction profile in the direction perpendicular to the flame with the calculated results at room temperature on both sides and 30% methane diluted by nitrogen, showing good reproducibility and good agreement. The flame was defined as a blue reaction zone in the experiments and the flame position in calculated results was defined as a maximum position of CH concentration. Fig. 4 shows NO and NO_2 mole fraction under the same conditions as those of Fig. 3. The calculated profile of NO has a maximum around the flame, but the experimental results have two maxima on both sides of the flame. Also, the NO_2 profile is completely reversed, that is, the calculated result has two maxima, as

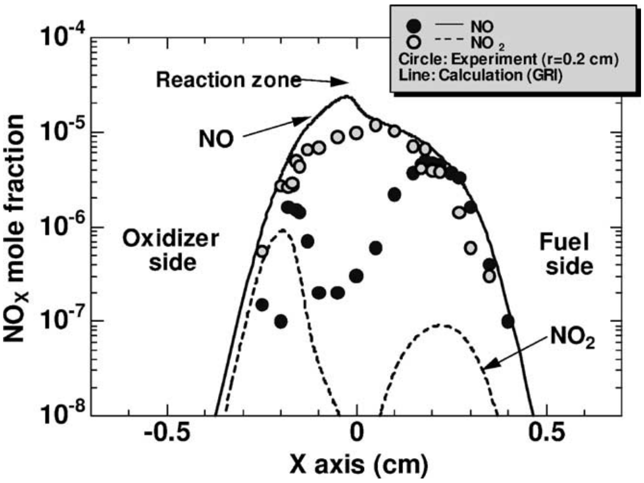


Fig. 4. Measured and calculated results of NO and NO_2 mole fraction (21% O_2, 30% CH_4, $T_0 = 294$ K, $\varepsilon = 50\ \mathrm{sec}^{-1}$).

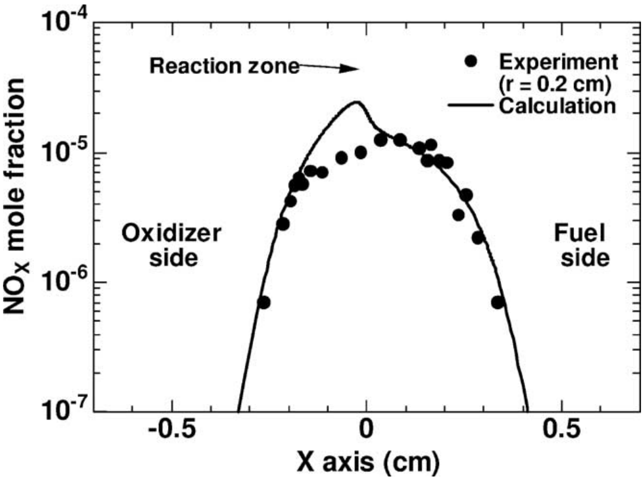


Fig. 5. The comparison of the total amount of measured NO_x $(= NO + NO_2)$ with the calculated one (21% O_2, 30% CH_4, $T_0 = 294$ K, $\varepsilon = 50\ \mathrm{sec}^{-1}$).

shown in the previous calculation by use of the diffusion flame in a two-dimensional jet [16], while the experimental results have one maximum.

These differences are suggested to be due to a rapid cooling of sampling gas to room temperature after it is sucked into the probe, because rapid cooling may result in transformation of NO to NO_2. Actually, the calculation by Kramlich et al. [17] predicted a rapid production of NO_2 under rapid cooling circumstances, and concluded that the transformation reaction from NO to NO_2 was promoted by the reaction between NO and the produced NO_2. The faster cooling speed, the greater the production of NO_2, and therefore a larger amount of NO might have been transformed into NO_2 in the present sampling since the present cooling speed was estimated to be a very fast value of 1000 $\mathrm{K \cdot m^{-1} \cdot s^{-1}}$.

The above-mentioned discussion leads to the conclusion that the experimental results of NO_2 in Fig. 4 are approximately equal to the profile of NO because the concentration of NO_2 should be generally one order smaller that of NO. However, we do not know how much NO was transformed into NO_2. Therefore, we should pay attention only to NO_x which is the total amount of NO and NO_2, instead of the value of NO or NO_2.

A rearrangement of data from Fig. 4 is shown in Fig. 5, showing sufficient agreement between calculations and experiments. The experimental data on the air side ($x = -0.15$ to 0), however, are smaller than the numerical results. The main reason is considered to be the temperature of the probe inlet, which is lower than the gaseous temperature in the high temperature region close to the flame. Because the production of NO_x depends strongly on temperature, the lower temperature might suppress the production of NO_x near the flame. The profiles of NO_x, however, sufficiently agree with each other as a whole, and we can conclude that the calculated results adequately predict the NO_x production rate.

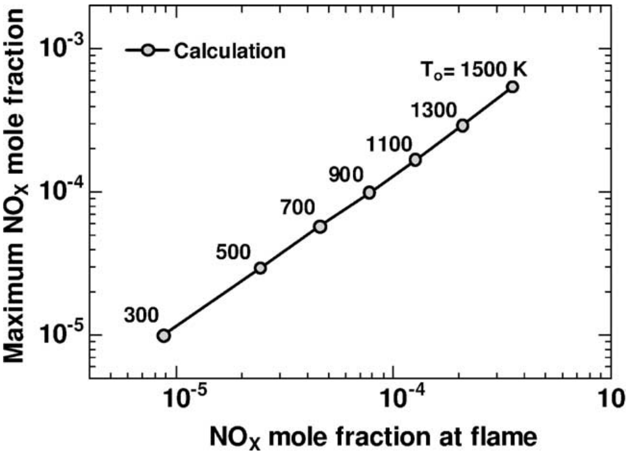


Fig. 6. The relationship between the NO_x mole fraction at the flame and that of the maximum value for various air temperature (T_0).

Fig. 6 shows the calculated results for the comparison of the maximum mole fraction of NO_x with the mole fraction of NO_x at the flame. Also, the further calculated results showed that the profile of NO_x changed in a similar manner when we changed the air temperature or the oxygen concentration in air. This linear relationship shown in Fig. 6 demonstrates that the mole fraction of NO_x at the flame can be taken as representative of NO_x production for a concerned flame. Accordingly, the mole fractions of NO_x at the flame are hereafter measured for the counterflow diffusion flame using high-temperature air.

Fig. 7 shows the variation of the mole fraction of NO_x with the temperature of preheated air, indicating a drastic decrease of NO_x at a relatively low oxidizer temperature due to the decrease of oxygen concentration from 21% to 15%. Agreement of experimental findings with calculations in the small mole fraction region is very difficult, because the measurements and the predictions of a small amount of NO_x tend to cause a large error. Therefore, experiments of low

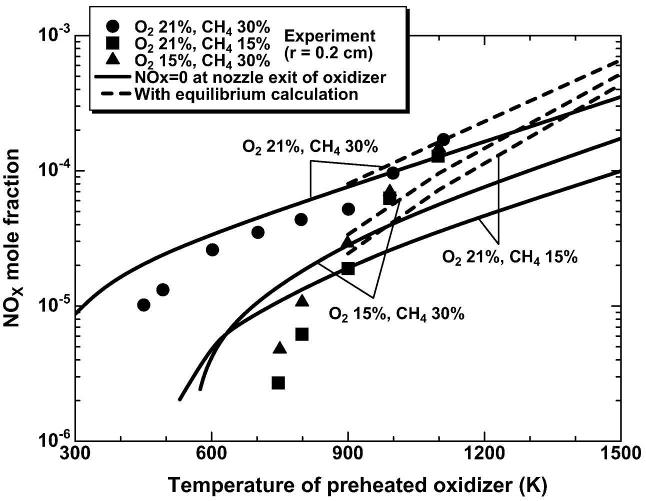
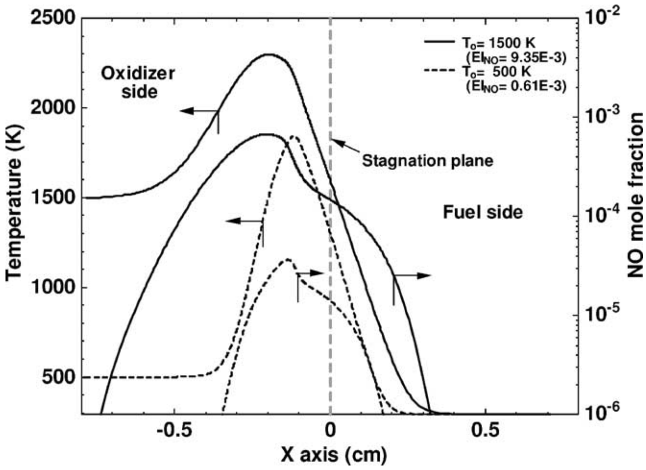


Fig. 7. The variation of NO_x mole fraction with the temperature of preheated oxidizer for various initial fuel and oxygen concentrations, at $\varepsilon = 150\ \text{sec}^{-1}$.

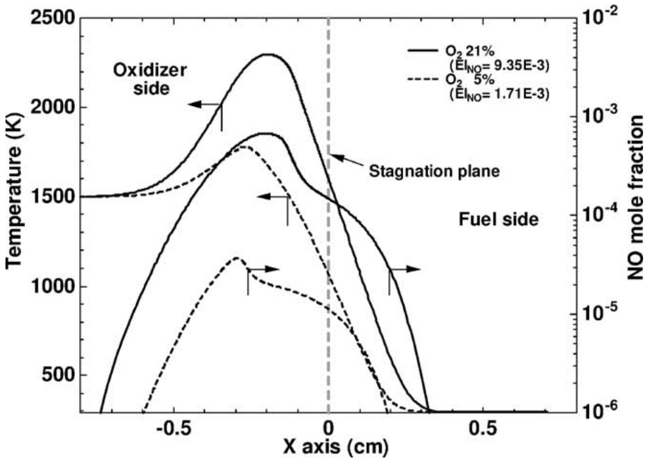
oxygen concentration which would result in very low NO_x had to be abandoned, although a lower oxygen concentration such as 5% was preferable as an experimental condition when we consider the practical usage of furnaces.

On the other hand, in the highly preheated oxidizer region in Fig. 7, the oxidizer itself should contain an appreciable amount of NO_x because of the production of thermal NO_x. The dashed line in Fig. 7 represents the mole fraction of NO_x, taking the original NO_x of hot oxidizer into consideration in the calculation, while the solid line denotes NO_x assuming zero NO_x in the fresh oxidizer. Since the hot air has a comparatively long residence time estimated to be about 1 sec in the present air preheater, the chemical equilibrium condition was assumed when the initial value of NO_x was calculated. This is the reason why the effect of oxygen concentration was not so large at high air temperature. The residence time of the fresh air with high temperature is estimated to be as short as several milliseconds in actual industrial furnaces. However that may be, the overall tendency of the experimental results is considered to be consistent with the predicted values. Thus, we can conclude that the calculation can predict NO_x emission qualitatively and also quantitatively on the whole.

Based on these considerations, a further calculation of NO emission was done for the case of high-temperature air. Fig. 8(a) shows a large increase of NO when we increased the air temperature from 500 K to 1500 K, keeping the other conditions constant. Fig. 8(b), however, shows a large decrease of NO when we decreased the oxygen concentration in air from 21% to 5%, keeping the air temperature at 1500 K. The emission index (EI) [11], as indicated in Fig. 8, decreased less than 1/5. This was due to the decreases of the flame temperature as seen in Fig. 8(b), as well as to the low concentration of oxygen. In the calculation of Fig. 8, thermal NO_x produced in air preheater was not added because the residence time in actual heat exchange media of industrial furnaces is very short, as mentioned above.



(a)



(b)

Fig. 8. (a) The comparison of NO_x profile at room air temperature with that at air temperature of 1500 K, 21% O_2, 30% CH_4 and $\varepsilon = 100\ \text{sec}^{-1}$. (b) The comparison of NO_x profile at 21% oxygen with that at 5% oxygen in air, keeping the air temperature of 1500 K constant, 300% CH_4 and $\varepsilon = 100\ \text{sec}^{-1}$.

In Fig. 8, oxygen is diluted by nitrogen. Effective NO emission should be smaller in actual industrial furnaces because air is diluted by flue gas containing abundant CO_2 and H_2O as well as N_2, which does not produce NO compared with the case of pure nitrogen as a diluent and also has a large radiation emissivity which evens the temperature around the flame.

The chemical reaction mechanism in high-temperature air combustion has been discussed in a previous report [17], in which a diffusion flame was used in a two-dimensional laminar jet. The increase of air temperature greatly enhanced the HCN → NH → NO route, in particular, the HCN → CN and NO → CN paths. The thermal mechanism rapidly converted NO back to N_2 at the flame zone, but quickly produced NO on the high-temperature air side. The fundamental

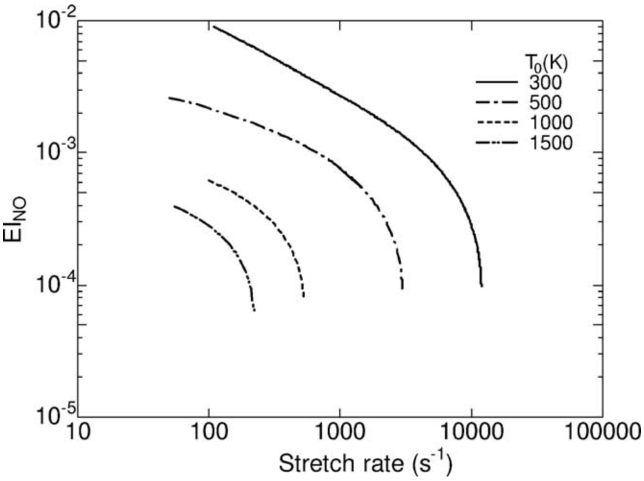


Fig. 9. The variation of the NO_x mole fraction with the stretch rate for various air temperatures (21% O_2, 30% CH_4).

mechanism of the NO_x chemical reaction, however, have not changed drastically even though high-temperature air was used.

One more point must be considered when we estimate the NO emission of actual furnaces. To make up for the low-oxygen concentration of air diluted by flue gas, a high velocity of airflow is used to increase an oxygen supply which may induce a strong turbulence. Thus, the effect of the stretch rate on NO emission was calculated for purpose of verification to evaluate the effect of turbulence, as seen in Fig. 9. Fig. 9 shows the overall emission characteristics of NO_x, the emission index (EI), which is the total emission of NO_x per unit mass of fuel consumed. The results show that the NO emission decreased sharply as the stretch rate increased. This was due to a decrease of residence time in the high-temperature region around the flame. This result may not demonstrate the whole aspect of the effect of turbulence on low NO_x emission in actual furnaces, but the present calculation by use of the counterflow diffusion flame certainly verifies the fundamental mechanisms or phenomena of low NO_x emission.

5. Conclusion

Experimental and numerical studies were carried out using counterflow diffusion flame to investigate the reason for low NO_x emission in the system employing high-temperature air with a low concentration of oxygen, which is recently being used in industrial furnaces. The following conclusions can be made:

(1) Although NO and NO_2 concentration cannot be measured separately by the present gas sampling system, the measured total amounts of NO_x $(= NO + NO_2)$ were sufficiently consistent with the predicted values.

(2) A drastic decrease of NO_x was obtained even in high air temperature by decreasing the oxygen concentration experimentally as well as numerically. At higher air temperature, however, the air itself produced thermal NO_x in the present laboratory-scale preheater, and it was therefore difficult in the present experiment to show the effective decrease of NO_x at higher air temperature, being different from actual furnaces.

(3) It was numerically found that a further decrease of oxygen in air caused a very large decrease of NO_x emission even if the air temperature was higher. Also, a drastic decrease of NO_x with the increase of stretch rate was shown numerically. This suggests the effectiveness of strong turbulence on the decrease of NO_x in actual industrial furnaces.

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