Numerical Analysis of Diffusion Combustion of Coal-Gasified Fuel*

(Effect of Pressure on NO_x Formation)

Zhe XU**, Mikio SATO***,
Takeharu HASEGAWA*** and Toshimi TAKAGI****

Numerical computations are made of laminar jet diffusion flames taking into account detailed chemical kinetics and multicomponent diffusion and focusing on the effect of pressure and the amounts of hydrocarbon contained in the fuel on the NO_x formation processes and characteristics. In order to clearly distinguish between thermal NO_x and fuel NO_x originating from N₂ in the air and fuel N, respectively, and to elucidate the effects of interaction between thermal NO_x and fuel NO_x together with N-containing species, N-containing species originating from N₂ in air and fuel N and their reactions are distinguished in the computations. It was shown that (1) higher pressure results in a decrease in the amount of fuel NO formed and a increase in the amount of thermal NO formed, (2) the tendency of the decrease of the conversion rate of ammonia to fuel NO for high-pressure flames becomes more apparent when the fuel contains greater amounts of methane, (3) the effect of the destruction of thermal NO by N-containing species becomes more apparent for high-pressure flames as thermal NO concentration becomes high.

Key Words: Diffusion Flame, Numerical Simulation, Pressure Effect, Coal-Gasified Fuel, Nitrogen Oxides

1. Introduction

As a new technology in electric power generation using coal fuels, considerable attention has been focused on a coal-gasification combined cycle power generation system.

The coal-gasification combined cycle power generation system is composed of a coal gasifier, gas cleaning system, gas turbine system, steam turbine using a waste heat recovery system. In the coal gasifier, nitrogenous compounds contained in coal are converted to ammonia in the coal-gasified fuel and are supplied to the gas turbine combustor without being removed when the gas cleaning system is a hot one.

As is well known, ammonia contained in the fuel is converted to NO_x in the combustion process. Low-fuel NO_x combustion technology is one of the most important subjects in the development of gas turbine combustors using coal-gasified fuel^{(1),(2)}.

Experimental and analytical studies for investigating NO_x formation in diffusion or premixed flames⁽³⁾⁻⁽⁷⁾, as well as in combustors or furnaces⁽⁸⁾⁻⁽¹¹⁾, have long been performed by many researchers. However, in most studies, the fuels such as hydrogen, methane and propane or with ammonia or nitric oxide, are generally used.

On the other hand, in experiments or usual computations, fuel NO is calculated by subtracting thermal NO from total NO, where thermal NO is obtained from a flame without fuel N. However, in real flames, the formation and destruction processes of fuel and thermal NO are interrelated. In particular, when the thermal NO formation increases, the effect of interaction between the fuel and thermal NO, such that the thermal NO is destroyed by fuel N, is expected to become large.

In the present study, NO_x formation processes and characteristics in laminar jet diffusion flames of

* Received 27th February, 1997. Japanese original: Trans. Jpn. Soc. Mech. Eng., Vol. 62, No. 602, B (1996), p. 3689-3695 (Received 26th December, 1995)

** Thermofluid Dynamics Division, National Aerospace Laboratory, Tokyo 182, Japan

*** Thermal Engineering Department, Central Research Institute of Electric Power Industry, Yokosuka, Kanagawa 240-01, Japan

**** Department of Mechanical Engineering, Osaka University, Suita, Osaka 565, Japan

coal-gasified fuel are numerically investigated, focusing on the effects of pressure and amounts of hydrocarbon (CH_4) contained in the fuel. Computations are made taking into account detailed chemical kinetics⁽¹²⁾ and multicomponent diffusion. N-containing species originating from N_2 in air and $\text{N}(\text{NH}_3)$ in the fuel and their reactions are distinguished in the computations, which enables clear distinction of thermal NO_x and fuel NO_x originating from N_2 in air and fuel N, respectively, and the elucidation of the effects of interaction between thermal NO_x and fuel NO_x together with N-containing species.

2. Formulation and Numerical Procedure

Formulae are derived for the computations of axisymmetric laminar jet diffusion flames where gaseous fuel jet from a round tube nozzle is surrounded by coaxial air.

By considering flames in which the axial convective fluxes are much larger than diffusive fluxes, streamwise diffusion can be neglected, which allows the use of boundary layer conservation equations of mass, axial momentum, species and energy.

$$\frac{\partial}{\partial x}(\rho u) + \frac{1}{r} \frac{\partial}{\partial r}(r \rho v) = 0 \quad (1)$$

Momentum

$$\rho \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial r} \right) = - \frac{\partial p}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \mu \frac{\partial u}{\partial r} \right) + \rho g_x \quad (2)$$

Species

$$\rho \left(u \frac{\partial m_j}{\partial x} + v \frac{\partial m_j}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D_{jm} \frac{\partial m_j}{\partial r} \right) + R_j \quad (3)$$

Energy

$$\rho \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\lambda}{C_{pm}} \frac{\partial h}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left\{ r \sum_{j=1}^n \left(\rho D_{jm} - \frac{\lambda}{C_{pm}} \right) h_j \frac{\partial m_j}{\partial r} \right\} \quad (4)$$

In these equations, x and r represent the axial and radial coordinates, respectively; u and v , the axial and radial fluid velocities; ρ , density; h , enthalpy; m_j and h_j , the mass fraction and enthalpy of the j -th species; R_j , rate of species production by chemical reactions; μ , viscosity; λ , thermal conductivity; C_{pm} , specific heat of the mixture; D_{jm} , the effective diffusivity of the j -th species in the mixture; and n , the number of species. Radiant heat transfer, thermal diffusion and viscous dissipation are neglected in this analysis.

Density is obtained from the ideal-gas equation. Temperature T in the flame is related to enthalpy and species concentrations. The thermodynamic and transport properties are calculated using the CHEMKIN program^{(13)–(15)}.

Table 1 Standard composition of the fuel considered

Fuel species	vol %	Fuel species	vol %
CO	18.3	CO ₂	15.9
H ₂	6.9	N ₂	56.3
CH ₄	2.5	NH ₃	0.1
High heating value of the fuel HHV=4190kJ/m ³			
Low heating value of the fuel LHV=3950kJ/m ³			

The numerical integration method is based on that in Ref.(16). The conservation equations are discretized by a control volume method and a marching integration is performed.

The upstream computations boundary is set in the plane of the fuel nozzle tip. The fuel or air flows at the inner or outer parts of the nozzle rim. The axial velocity profile at the exit of the fuel nozzle is assumed to be parabolic and the profile of air flow outside the nozzle is flat. The radial velocity component is zero. The adiabatic equilibrium concentration of species and the temperature of a stoichiometric mixture of fuel and air are given at the fuel nozzle rim of 0.4 mm thickness to initiate the reactions. On the central axis, zero-gradient species concentration, temperature and velocity are given. At the outer tube wall, zero-gradient species concentration and temperature as well as the nonslip velocity condition, are given.

3. Coal-Gasified Fuel and Reaction Scheme

The main combustible components of the coal-gasified fuel produced by the air-blown entrained-bed coal gasifier are carbon monoxide (CO) and hydrogen (H_2). However, more than 60 percent of the fuel composition consists of inert gases such as nitrogen (N_2) and carbon dioxide (CO_2). The fuel also contains a small amount of methane (CH_4) and ammonia (NH_3). NH_3 will be converted to fuel NO_x in the combustion process. Since the coal-gasified fuel has a low heating value and contains a high percentage of inert gases, its flame temperature is relatively low. Table 1 shows the standard composition of the fuel considered⁽¹⁷⁾.

The scheme of the elementary reactions and their forward rate constants used in the computations are based on those in Ref.(12). The scheme consists of 383 pairs of elementary reactions.

A total of 49 species are considered: CH_4 , CH_3 , CH_3O , CH_2OH , CH_2O , CH_2 , CH , CO , CO_2 , C , H_2 , H , O , OH , O_2 , H_2O , HO_2 , H_2O_2 , N_2 , HCO , CH_2CO , C_2H , C_2H_2 , C_2H_3 , C_2H_4 , C_2H_5 , C_2H_6 , HCCO , HCCOH , C_3H_2 , C_4H_2 , N , NO , NO_2 , N_2O , N_2H_2 , HCN , CN , H_2CN , NH_3 , NH_2 , NH , NNH , HNO , HCNO , HOCN , HNCO , NCO , C_2N_2 .

Fig. 1 Schematic diagram of the formation processes of thermal NO(NO^t) and fuel NO(NO^f)

NO_x is formed both from any fuel-nitrogen (fuel N) species (called fuel NO_x) and from N_2 (called thermal NO_x) by the reactions related to N-containing species, which occur in parallel with the combustion reactions. The fuel NO_x coexists with thermal NO_x in the flame and it is difficult to distinguish between them in experiments or in conventional computations because no physical or chemical difference exists between them. In the present study, in order to investigate the characteristics of fuel NO_x and thermal NO_x formation and the effect of intervention between them, the reaction processes of the fuel and thermal NO formation are separately considered, as shown in the schematic diagram in Fig. 1.

In the present computations, thermal NO and fuel NO originating from N_2 in the air and NH_3 in the fuel are denoted NO^t and NO^f , respectively. All N-containing species whose N element comes from N_2 or NH_3 are denoted by adding suffix t or f, e.g., NO^t and NO^f . This method enables us to discriminate the origin of the N element in all species and to directly evaluate thermal NO(NO^t) and fuel NO(NO^f) formation, even though the chemical and physical properties are the same.

4. Results and Discussion

4.1 Structure of the flames and characteristics of NO_x formation

The conditions for the flames are as follows. The inner diameter of the fuel nozzle is 4.2 mm. The surrounding coaxial air comes from the air tube of 7.0 mm diameter. The average velocity at the fuel nozzle exit and the surrounding average air velocity are 4.0 and 1.7 m/s, respectively. The average excess air ratio (air flow rate divided by stoichiometric air flow rate) is 1.2 and inlet temperatures of fuel and air are 600 K. The ambient pressure is selected to be 0.1, 0.5 or 1.0 MPa. An axisymmetric, laminar diffusion flame is formed in a 7.0 mm-inner-diameter tube.

Figures 2 and 3(a) and (b) show radial profiles of temperature and species concentration in the flames using the standard composition of fuel at the cross section at $x=10$ mm ($p=0.1$ MPa) and at the cross sections at $x=10$ and 50 mm ($p=0.5$ MPa), respectively.

x and r are axial distance from the nozzle tip and radial distance from the central axis, respectively.

Figures 4 and 5 show the radial profiles of fuel NO and thermal NO, respectively, at various cross sections in flames of 3 different ambient pressures P of 0.1, 0.5 and 1.0 MPa.

For the two flames of different pressures shown in Figs 2 and 3, the following are noted with respect to the flame structure and configuration.

(1) High concentrations of H, OH and O radicals are found near the high-temperature stoichiometric region. NH_3 is decomposed to form intermediate products NH_i ($i=0,1,2$) in the fuel-rich side and then to form NO near the stoichiometric region. The concentrations of NH_i have peaks in the fuel-rich side near the stoichiometric region.

(2) Hydrocarbon (CH_4) contained in the fuel induces the formation of the intermediate product of HCN in the fuel-rich side. This is mainly attributed to two reaction processes: one is the reaction of CH_i with NH_i to form HCN, and the other is the diffusion of NO into the fuel-rich region and its subsequent decomposition to form HCN. HCN is decomposed into NH_i in a region closer to the stoichiometric condition as compared with the case of NH_3 . As is well known, NH_i is easily converted to NO if it is formed near the stoichiometric flame front. This may be the main reason why the NO_x formed is higher in the flames when the fuel contains CH_4 , as shown in Fig. 7.

The effects of pressure are as follows.

(3) The flame temperature is considerably higher for a higher-pressure flame. The maximum adiabatic flame temperature of the original fuel with air is about 1 832.3~1 840.0 K irrespective of the pressure. The maximum flame temperature observed in the higher-pressure flame is higher than the adiabatic flame temperature of the original fuel, which was caused by the effect of the preferential diffusion of heat and species. The effect of preferential diffusion of heat and species becomes more apparent at higher pressure^{(18),(19)}.

(4) The radial widths of temperature and species concentration profiles decrease with higher pressure when they are compared at the cross section of the same axial distance. This is due to the decrease of the diffusion coefficients and the increase of the reaction rates at higher pressure.

(5) The flame length is nearly proportional to pressure when the velocities at the exit of the fuel nozzle are the same for various pressures, because diffusion coefficients are inversely proportional to pressure.

(6) The concentrations of H, OH and O radicals

as well as the concentrations of the NH ($i=0,1,2$) and HCN intermediate products become lower for higher-pressure flames.

As for the characteristics of fuel NO and thermal NO shown in Figs. 4 and 5, the following are noted.

(1) Fuel NO (NO^f in the figures) dominates total

Fig. 2 Radial profiles of temperature and species concentration in flame, $x=10$ mm ($p=0.1$ MPa)

Fig. 3 Radial profiles of temperature and species concentration in flame ($p=0.5$ MPa)

NO (NO in the figures) at atmospheric pressure (0.1 MPa). For the higher-pressure flame, the amount of fuel NO becomes lower. This is because the concentrations of H, OH and O radicals decrease.

(2) Although, the amount of thermal NO^t(NO^t-

NO^t) formation is very low with low flame temperature at atmospheric pressure, its concentration increases for higher-pressure flames because (a) higher pressure induces higher flame temperature due to the preferential diffusion, and (b) higher pressure results in higher reaction rates because of the higher molecular density.

Figures 6(a) and (b) show the axial profiles of the conversion rates of NH₃ to NO and HCN in flames of 0.1 and 0.5 MPa, respectively. The conversion rate

Fig. 4 Radial profiles of fuel NO(NO^f)

Fig. 5 Radial profiles of thermal NO(NO^t)

(C.R.) at each section is defined as the flow rate of N contained in the nitrogen-containing species divided by the flow rate of N contained in the original fuel. HCN is converted from fuel N not too far from the nozzle, reaches a maximum level and then decays rapidly along with the flow during mixing with excess air when NO reaches a maximum level and maintains its value downstream, as shown in the case of the atmospheric-pressure flame.

For the higher-pressure flame, the same tendency

Fig. 6 Axial profiles of the conversion rates of NH_3 to NO, HCN and NH_3

Fig. 7 Effect of pressure on the conversion rate of NH_3 to NO

is observed, but the conversion rates of NH_3 to NO and HCN are much lower than in the lower-pressure case.

Figure 7 shows the characteristics of fuel NO emission from NH_3 in the fuel, as the ambient pressure changes. The horizontal axis represents the pressure, and the vertical axis represents the conversion rate of NH_3 to NO. The concentration of NH_3 in the fuel is fixed at 1 000 ppm. Furthermore, the concentration of CH_4 in the fuel is changed within the range of 0.0 percent to 2.5 percent. The conversion rate of NH_3 to NO decreases when the pressure increases from 0.1 to 1.0 MPa. This tendency becomes more apparent when the concentration of CH_4 increases. The reason for this is the formation of the intermediate product HCN which is liable to convert to fuel NO. At the higher pressure, the amount of HCN formed decreases and the amount of fuel NO formed by way of the HCN becomes smaller. In other words, the dependence of the conversion of NH_3 to fuel NO on CH_4 becomes weaker when pressure becomes higher.

4.2 Characteristics of intervention between fuel NO and thermal NO

In the present study, fuel and thermal NO formation is calculated separately by labeling N-containing species using the suffix as f and t for N atoms originating from fuel N and N_2 in the air, respectively.

Figure 8 shows the radial profiles of thermal NO concentration at various cross sections in the flames of 0.5 MPa. The profile of thermal NO originating from N_2 (NO^t) is shown by the solid lines, while that of thermal NO obtained in the flame without fuel N (NO^*) is shown by the broken lines.

Figure 8 shows that the concentration of NO^t is smaller than that of NO^* . This indicates that thermal

Fig. 8 Radial profiles of thermal NO in flames ($p=0.5$ MPa)

Solid lines: Thermal NO from N_2

Broken lines: Thermal NO from the flame without fuel N

Fig. 9 Effect of pressure on the conversion rate of NH_3 to NO ($\text{CH}_4=2.5\%$)

Solid lines: Fuel NO from fuel N

Broken lines: Fuel NO calculated by subtracting the amount of thermal NO from the total amount of NO obtained in the flame without fuel N

NO destruction reactions are promoted by the existence of fuel N. The main interactions between thermal NO and fuel N are

The amount of fuel NO obtained by subtracting the amount of NO^* from the total amount of NO underestimates the actual amount of fuel NO in the flames.

Figure 9 shows the dependence of the conversion rate of NH_3 to NO on pressure when the CH_4 concentration in the fuel is fixed at 2.5 percent. For the case where fuel NO is defined as NO from fuel N, the conversion rate of NH_3 to NO is shown by the solid line. For another case where the amount of fuel NO is calculated by subtracting the amount of NO^* from the total amount of NO, the conversion rate is shown by the broken line. It is noted that when the pressure is raised, the difference between the solid and broken line becomes substantial. This indicates that fuel NO, as well as the conversion rate of NH_3 to NO, will be strongly influenced by thermal NO destruction processes by fuel N, especially when thermal NO concentration is high at high pressure.

5. Conclusions

Numerical computations of laminar diffusion flames of coal-gasified fuel were carried out by taking into account detailed chemical kinetics and multicomponent diffusion, focusing on the effects of pressure and amounts of hydrocarbon (CH_4) contained in the fuel on the NO formation processes and characteristics. N-containing species from N_2 in air and fuel N (NH_3) and their reactions are distinguished which enabled the elucidating of the effects of interaction between thermal and fuel NO together

with N-containing species.

The results are as follows.

(1) The amount of fuel NO formed, as well as the conversion rate of NH_3 to NO, decreases in high-pressure flames. The cause is mainly the lower concentration of radical species at higher pressure.

(2) The amount of thermal NO formed increases at higher pressure because of the higher temperature due to preferential diffusion effects and higher molecular density which enhance the NO formation reactions at higher pressure.

(3) The methane contained in the fuel plays an important role in the process of NO_x formation in relation to HCN formation and destruction in the flame. The conversion rate of ammonia to fuel NO is higher for a flame with a higher concentration of methane. The conversion rate significantly decreases for a higher-pressure flame and the degree of decrease is much greater for the flame of methane-containing fuel.

(4) The effect of interaction between fuel NO and thermal NO and N-containing species is substantial. The effect of the destruction of thermal NO by N-containing species becomes more apparent for high-pressure flames when thermal NO concentration becomes large.

References

- (1) Sato, M., Ninomiya, T., Nakata, T., Yoshine, T., Yamada, M. and Hisa, S., ASME paper, 90-GT-381 (1990).
- (2) Nakata, T., Sato, M., Ninomiya, T. and Hasegawa, T., ASME paper, 94-GT-218 (1994).
- (3) Fenimore, C.P., Effects of Diluents and Mixing on Nitric Oxide from Fuel-Nitrogen Species in Diffusion Flames, Sixteenth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1977, p. 1065-1071.
- (4) Takagi, T., Ogasawara, M., Daizo, M. and Tsumi, T., NO_x Formation from Nitrogen in Fuel and Air during Turbulent Diffusion Combustion, Sixteenth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1977, p. 181-189.
- (5) Vranos, A., Knight, B.A., Proscia, W.M., Chiappetta, T. and Smooke, M.D., Twenty-Fourth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1992, p. 377-384.
- (6) Nishioka, M., Nakagawa, S., Ishikawa, Y. and Takeno, T., Combust. Flame Vol. 98 (1994), p. 127-138.
- (7) Correa, S.M. and Smooke, M.D., NO_x in Parametrically Varied Methane Flames, Twenty-Third Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1990, p. 289.
- (8) Mizutani, Y. and Katsuki, S., Bull. JSME, (in Japanese), Vol. 42 (1976), pp. 943-948.
- (9) Clark, W.D., Folsom, B.A., Seeker, W.R. and

- Courtney, C.W., Transactions of the ASME, Vol 120 (1982), p. 104.
- (10) Michaud, M.G., Westmoreland, P.R. and Feitelberg, A.S., Chemical Mechanisms of NO_x Formation for Gas Turbine Conditions, Twenty-Fourth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1992, p. 879-887.
 - (11) Yamagishi, K., Nozawa, M., Yoshie, T., Tokumoto, T. and Kakegawa, Y., Fifteenth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1975, p. 1157-1166.
 - (12) Miller, J.M. and Bowman, C.T., Mechanism and Modeling of Nitrogen Chemistry in Combustion, Prog. Energy Combust. Sci., Vol. 15 (1989), p. 287-338.
 - (13) Kee, R.J., Rupley, F.M. and Miller, J.A., Sandia Report SAND 89-8009 B, 1993.
 - (14) Kee, R.J., Dixon-Lewis, G., Warnatz, J., Coltrin, M.E. and Miller, J.A., Sandia Report SAND 86-8246, 1993.
 - (15) Kee, R.J., Rupley, F.M. and Miller, J.A., Sandia Report SAND 87-8215, 1990.
 - (16) Spalding, D.B., HMT Genmix-A General Computer Program for Two-Dimensional Parabolic Phenomena, Pergamon, New York, (1977).
 - (17) Nakata, T., Sato, M. and Hasegawa, T., Formation Characteristics of Fuel NO_x in the Combustion of Coal Gaseous-Fueled Gas Turbine, Bull. JSME, (in Japanese), Vol. 59 (1993), p. 2568-2575.
 - (18) Takagi, T. and Xu, Z., Numerical Analysis of Laminar Diffusion Flames-Effects of Preferential Diffusion of Heat and Species, Combust. Flame, Vol. 96 (1994), p. 50-59.
 - (19) Xu, Z. and Takagi, T., Numerical Prediction of Pressure Effects on Diffusion Flames, Bull. JSME, (in Japanese), Vol. 62 (1996), p. 776-782.