

NUMERICAL MODELING OF NITROUS OXIDE FORMATION FROM CHAR COMBUSTION

**Atsushi Morihara, Claes J. Tullin,
J. Derek Teare, Adel F. Sarofim and János M. Beér**
*Department of Chemical Engineering
and
Energy Laboratory
Massachusetts Institute of Technology
Cambridge, MA 02139*

Keywords: coal, nitrous oxide and heterogeneous reaction

ABSTRACT

Growing scientific and public concerns over global warming and ozone layer depletion have led researchers to study the causes for the observed increase in ambient N₂O concentrations. Man made sources, such as N₂O emissions from fossil fuel combustion, have been implicated. However, the mechanism for N₂O formation in coal combustion is not fully understood. It is especially difficult to deal with N₂O formation since the reactions are complex. In this paper, a model for NO and N₂O formation and destruction using a single particle model is discussed. The model is based on the experimental observation that the formation of N₂O is dependent on the existence of both NO and O₂ in the system. Numerical simulations, using the control volume method, show the effects of particle diameter and pressure. The results of the model are compared with experimental data, and show good agreement.

INTRODUCTION

Potential anthropogenic sources of N₂O that have been investigated include fossil fuel combustion. Until recently, pulverized-coal combustion was implicated as the main source of N₂O emission due to errors encountered in sampling. It is now known that emissions from these units are typically less than 10 ppm. Fluidized bed combustion (FBC) has emerged as an advanced method of energy production, but for current designs these units have been shown to emit more N₂O than their pulverized-coal combustion counterparts[1].

In fluidized bed combustion, the emission of N₂O formed from char decreases with increasing temperature, in contrast to the trend for char NO emissions that increase or pass through a maximum with increasing temperature[2][3]. The char nitrogen conversion to NO as a function of temperature has been determined by Yue using an analytical solution[4]. Yue's approach is based on first order kinetics. The complex N₂O reactions, however,

preclude an analytical solution, and a numerical approach is indispensable for calculating the fraction of the char nitrogen converted to N₂O.

The mechanism used in this paper is an extension of that developed by de Soete[5] in which it is postulated that (-CN) reacts with O₂ to form (-CNO) and the (-CNO) next reacts with NO to form N₂O. The (-CNO) can also dissociate to form NO.

FUNDAMENTAL EQUATIONS

The fundamental reactions leading to NO and N₂O formation and destruction are considered to be:



NO and N₂O are mainly reduced heterogeneously by carbon. The formation reaction rates of NO r_{NO} and that of N₂O r_{N_2O} are given by:

$$r_{NO} = k_2 [(-CNO)] \quad (6)$$

$$r_{N_2O} = k_3 [NO] \cdot [(-CNO)] \quad (7)$$

The fractions of char-nitrogen transformed into NO and N₂O has been shown to be roughly proportional to the fraction of carbon burnt[4]. The total nitrogen oxidation rate, f_N , is therefore equal to the product of N/C ratio and reaction rate of carbon oxidation, f_C :

$$f_N = r_{NO} + 2 \cdot r_{N_2O} = \frac{N}{C} f_C \quad (8)$$

f_C in turn is calculated using reaction rate information from Smith[6]. By manipulating Eqs.(6), (7), and (8), the concentration of (-CNO) can be shown to be:

$$[(-CNO)] = \frac{\frac{N}{C} f_C}{k_2 + 2 \cdot k_3 [NO]} \quad (9)$$

If we replace (-CNO) in Eqs.(6) and (7) by Eq.(9), the reaction rates of NO and N₂O are given by:

$$r_{NO} = \frac{N}{C} f_c \cdot (1 - 2\alpha) \quad (10)$$

$$r_{N_2O} = \frac{N}{C} f_c \cdot \alpha \quad (11)$$

where

$$\alpha = \frac{k_3[NO]}{k_2} \left(1 + 2 \cdot \frac{k_3[NO]}{k_2} \right)^{-1} \quad (12)$$

If the NO concentration is small enough, Eqs.(10) and (11) become:

$$r_{NO} = \frac{N}{C} f_c \cdot (1 - 2 \cdot k_3[NO]) \quad (13)$$

$$r_{N_2O} = \frac{N}{C} f_c \cdot k_3[NO] \quad (14)$$

$$k_r = k_3 / k_2 \quad (15)$$

k_r is a function only of temperature. If the reaction rate of carbon oxidization is proportional to O₂ concentration, then the rate of conversion of nitrogen in the char to N₂O is proportional to the NO and O₂ concentrations, and the rest of the nitrogen in the char is converted to NO.

CALCULATION

A material balance on a spherical shell in the carbon particle yields:

$$De_i \frac{1}{r^2} \left(r^2 \frac{\partial}{\partial r} C_i \right) + f_i(C_1, C_2, \dots) = 0 \quad (16)$$

where C_i is the concentration of the i th species, where i can be O₂, CO, CO₂, NO, and N₂O. De_i represents the effective diffusivity of component i calculated on the basis of Knudsen diffusion within the pores of the char particle. r is radial distance from the center of the particle. $f_i(C_1, C_2, \dots)$ is the reaction term. The boundary conditions are given by:

$$-De_i \frac{\partial C_i}{\partial r} \Big|_{r=R_p} = k_m (C_i|_{r=R_p} - C_i|_{r \rightarrow \infty}) \quad (17)$$

where k_m is the external mass transfer coefficient and R_p is the particle radius[7][8].

Figure 1 shows the calculation cell of the particle, which is a portion of the spherical shell. To allow for the concentration of the reaction near the particle surface, the shell thickness decreases with increasing radius. The destruction and formation reactions are assumed to be uniformly distributed in a cell volume, and

diffusion between cells is formulated at each cell surface. For the exterior cell the diffusion to the surface is equated to the external mass transfer.

An example of a typical concentration profile is shown on the same figure. O₂ is consumed near the surface of the particle. NO is also formed in this region, and it either diffuses towards the center of the particle where it reacts with the char or it diffuses to the surface where it escapes from the particle. As a result, the NO concentration in the particle is depleted at the center of the particle where the NO consumption reactions prevail, increases to a maximum nearer the surface where the NO is produced, and falls at the surface due to the NO diffusion out of the particle. N₂O is formed at the same time as NO at a rate proportional to the local NO concentration. Part of the N₂O is also destroyed in the particle by reaction with carbon. Because the N₂O destruction rate is low the N₂O concentration can increase with decreasing radius.

EXPERIMENTAL

Batch combustion experiments were performed in a small scale quartz glass bubbling fluidized bed reactor (inner diameter 57 mm). A bed of Silica sand (particle size 150-212 μm), with a bed height of approximately 50 mm, was fluidized by a mixture 8 % O₂ in helium. The composition and flow rate were controlled using mass flow controllers. The flow rate was set to 2.5 l/min NTP (273 K 1 atm). In each experiment, coal particles (diameter 4 mm) were burned. The concentrations of the combustion products, N₂O, NO, O₂, CO₂, CO, and CH₄, were obtained using a FTIR spectrometer equipped with a MCT detector, and a low volume (223 cm²) gas cell with variable path length, which was set to 7.25 m in the experiments discussed here. A detailed description of the reactor and experimental set-up can be found elsewhere[9].

The fractions of char nitrogen converted to NO and N₂O as functions of carbon conversion can be calculated from the concentrations and gas flow rate. The instantaneous conversions to NO and N₂O are given by:

$$f_{N_2O} = \frac{2[N_2O]}{\frac{N}{C} \sum ([CO_2] + [CO] + [CH_4])} \quad (18)$$

$$f_{NO} = \frac{[NO]}{\frac{N}{C} \sum ([CO_2] + [CO] + [CH_4])} \quad (19)$$

COMPARISON

The effect of particle radius on the fraction of fuel nitrogen converted to NO and N₂O is shown in Figure 2. These calculations were performed by assuming a shrinking particle model. The calculated conversions to NO and N₂O, which are functions of the shrinking sphere radius, are compared with the data. The conversion to NO decreases with increasing radius, while the conversion to N₂O

increases. The calculated results show the formation and destruction of both NO and N₂O. The ratio of N₂O formation rate to total rate increases with increasing radius, since the NO concentration in the pore increases with increasing radius.

With the model in this way effectively validated by comparison with data at atmospheric pressure, it is reasonable to use it for prediction of behavior at higher pressures. For example, one can calculate the effect of decrease in the external mass transfer coefficient due to increase in pressure. The effect of this is shown in Figure 3. The conversions of the fuel nitrogen to NO and N₂O can be shown, from consideration of the governing equations, to be functions of four dimensionless groups: three Thiele moduli $R_p\sqrt{k_{O_2}/D_e}$, $R_p\sqrt{k_{NO}/D_e}$, $R_p\sqrt{k_{N_2O}/D_e}$, and the Biot number $k_m R_p/D_e$, where k_{O_2} , k_{NO} , and k_{N_2O} are the rate constants for the reactions of O₂, NO, and N₂O with char, k_m is the external mass transfer coefficient, and D_e the effective diffusivity in the pores of the particle. Only k_m is a function of pressure since it is directly proportional to the bulk gas diffusivity, which in turn is inversely proportional to pressure. The model can therefore be used to predict the effect of pressure by varying the Biot number. These results, for representative values of the Thiele moduli, are shown in Figure 3. The predicted results show that NO decreases with increased pressure, consistent with the limited available measurements.

Thus the model, based on comparatively simple formation and destruction mechanisms, yields good agreement between experimental data and the calculation results.

CONCLUSION

For the conditions studied (a Newland, Australia bituminous coal) as the char conversion increases, the conversion of char nitrogen to NO increases, approaching one in the limit, while that to N₂O decreases with decreasing radius.

The results can be well modeled by assuming that, as the char is oxidized, the associated char nitrogen is converted to either N₂O or NO, with the split depending on the local NO concentration, and that there is a subsequent partial reduction of the NO and N₂O as these species diffuse through the porous char to the particle surface.

REFERENCES

1. M. D. Mann, M. D. Collings, and E. B. Botros "Nitrous Oxide Emissions in Fluidized-bed Combustion: Fundamental Chemistry and Combustion Testing." *Prog. Energy Combust. Sci.* 1992, Vol.18, pp. 447-461
2. Atsushi Morihara, Claes J. Tullin, Adel F. Sarofim and János M. Beér "Oxidization of Char Nitrogen: Extrapolation of Results from Fluidized Bed Reactors to Pulverized Coal Flames" 7th Topic Oriented Technical Meeting, May 1993

3. Claes J. Tullin, Adel F. Sarofim and János M. Beér "NO and N₂O Formation for Coal Combustion in a Fluidized Bed: Effect of Carbon Conversion and Bed Temperature" (Submitted to Energy & Fuel, April 1993)
4. G. X. Yue, F. J. Pereira, Adel F. Sarofim and Janós M. Beér, "Char Nitrogen Conversion to NO_x in Fluidized Bed", Combustion Science and Technology, 1992. Vol. 83, pp. 245-256
5. G. G. de Soete "Heterogeneous N₂O and NO Formation from Bound Nitrogen Atoms during Coal Char Combustion" Twenty-Third Symposium (International) on Combustion, 1990, pp. 1257-1264
6. I. W. Smith "The Combustion Rates of Coal Chars: A review" Ninth Symposium (International) on Combustion Institute, 1982, pp. 1045-1065
7. Octave Levenspiel "Chemical Reaction Engineering" Second Edition, John Wiley & Sons, Inc. pp. 357-401, 1972
9. Claes J. Tullin, Adel F. Sarofim and János M. Beér "Formation of NO and N₂O in Coal Combustion: The Relative Importance of Volatile and Char Nitrogen" 12 th International Conference on Fluidized Bed Combustion, pp. 599-609, May 1993

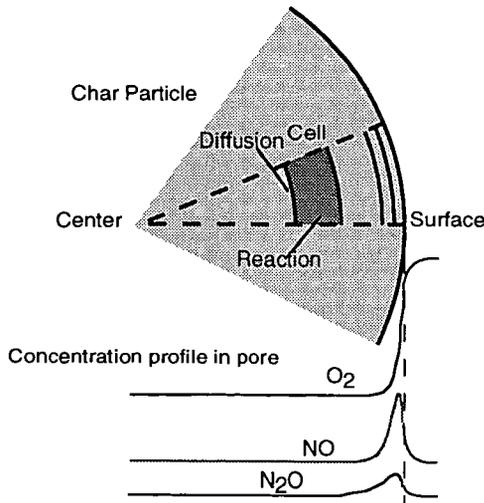


Figure 1 Calculation method and concentration profiles in the particle

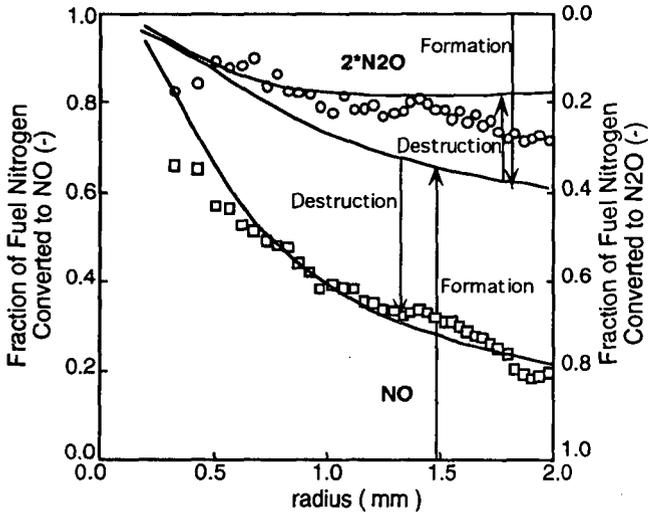


Figure 2 Effect of particle radius on char nitrogen conversion rate to NO and N2O

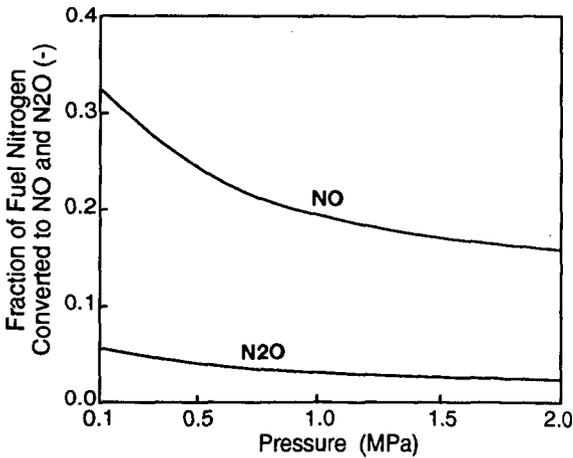


Figure 3 Effect of pressure on char nitrogen conversion rate to NO and N2O