Prediction of Nitric Oxide in Advanced Combustion Systems

Richard D. Boardman,
L. Douglas Smoot
Chemical Engineering Department
Brigham Young University
Provo, UT 84602

A computer model to predict nitric oxide (NO) concentrations has been applied to advanced-concept pulverized coal systems and evaluated by comparing model predictions with experimental data. Specifically, the effects of pressure, stoichiometric ratio, air stage location, temperature, and inert gas type on NO concentrations were predicted by the model and compared to experimental data. This work is a continuation of previous model evaluations, which found favorable prediction of NO concentrations for variation of stoichiometric air/fuel ratio, coal moisture content, particle size, and swirling and nonswirling diffusion flames (Hill et al., 1984; Smith et al., 1986).

The NO model is a subcomponent of a general combustion code that provides theoretical predictions for the temperature, velocity, major species, and other properties at local points throughout turbulent, combusting flow fields (Smoot and Smith, 1985). In the NO model, fuel nitrogen release from the coal is assumed to occur at a rate proportional to total coal weight loss. The volatile nitrogen is assumed to be instantaneously converted to HCN. NO is formed by oxidation of the HCN and is competitively reduced to N_2 by reaction with HCN. Global rate expressions for these reactions were measured by de Soëte (1975). The model also accounts for the destruction of NO by heterogeneous interaction with char using a rate expression from Levy et al., (1981). All rate parameters are used as reported except for the formation of NO. For this rate equation, the preexponential factor was increased by a factor of 10. This value is still within the range of experimental error and was used because it yielded better results. Effects of turbulence on the gaseous reactions are accounted for through use of a joint probability calculation of fluctuating gaseous and coal off-gas mixture fractions. These two progress variables are sufficient to track turbulent temperature and gas concentration variations (Smith et al., 1982). Experimental data sources for model comparisons were selected for axisymmetric combustion experiments that investigated the variation of key test variables (e.g., pressure or stoichiometric ratio, SR). Table 1 lists the combustion configurations, reactor dimensions, coal types, firing rates, and other parameters. Comparisons of predicted NO concentrations with experimental measurements were made after acceptable agreement for the main stream variables was demonstrated (Boardman, 1987).

Entrained-Flow Gasification

Four simulations of three coal types were completed. Figures 1 and 2 compare, respectively, the experimental and theoretical NO concentration profiles for atmospheric and high-pressure (5 atm) gasification of Utah bituminous coal. Predicted and measured peak NO concentrations are similar in magnitude and location. Predicted concentration contours closely match the experimental maps for the atmospheric case throughout the entire reactor, while the high-pressure case also matches the peak NO value but decays somewhat more slowly. A predicted exit concentration of 100 ppm is approximately 30% below the measured value for the atmospheric pressure case, while the predicted exit value of 4 ppm differs by only 2 ppm from the measured value for the high-pressure case.

Nonstaged, Air-Coal Combustion

Cases were simulated for nonstaged combustion at fuel-lean (SR = 1.20), near stoichiometric ratio (SR = 0.95), and fuel-rich (SR = 0.80) conditions. The measured data and predicted profiles are compared in Figure 3 for each case. For the fuel-lean case, a high peak NO concentration is predicted initially but the profile rapidly decays to approximately 8% above the experimental profile. A similar trend is predicted for the SR = 0.95 case except that the NO profile decays to a level 10–15% below the measured data. The predicted NO concentrations also follow this trend for the SR = 0.80 case but are consistently lower by 15–30% along the entire profile. The discrepancies between the measured and predicted NO concentrations in the early region of the reactor may be due to nonisokinetic sam-

---

Correspondence concerning this paper should be addressed to L. D. Smoot.

Table 1. Experimental Cases Selected for Model Evaluation

Combust. Config.*	Data Sources	No. Cases	Fig. Nos.	Coal Feed Rate kg/h	Reported NO Conc.	Parameters Investigated	Coal
Gasification $L = 1.89$ m $D = 0.2$ m	Brown et al. (1986); Nichols et al. (1987); Azuhata et al. (1986)	4	1, 2	35	2-D profile	Press. (1–5 atm); temp.	Utah bit.; Ill. subbit.; N.D. lig.
Nonstaged	Wendt et al. (1978)	3	3, 4	5	1-D profile	Stoich. ratio (0.8–1.2)	Ken. bit.
Air-staged $L = 2.2$ m $D = 0.15$ m	Wendt et al. (1978)	4	5	5	1-D profile	Secondary-air stage location (0.52–0.90 s)	Ken. bit.
CO_2-O_2 Oxidizer $L = 2.74$ m $D = 0.6$ m	Berry et al. (1986)	4	6	30–35	Effluent	CO_2-O_2 ratio	Colo. subbit.
Entrained-flow	Pershing (1977)	4	7	5	Effluent	Fuel NO temp. dependence	Colo. subbit.

*L = Reactor length; D = reactor diameter.

pling. The model predictions showed steep radial gradients in the early section of the reactor. In fact, the NO concentration profile predicted near the wall closely matched the experimental data throughout the entire reactor, including the early reactor region. A separate explanation for this discrepancy may be a result of assuming that fuel nitrogen is evolved at a rate proportional to the total coal mass loss. Wendt (1980) found that at low temperature the early volatiles are nitrogen-free. If the rate of nitrogen release is lower than the rate of total coal mass loss, then the model would overpredict the formation of NO in the near-burner region. Figure 4 compares the theoretical and experimental effluent NO concentrations over the range of stoichiometric ratios shown. The model closely predicts the measured effluent values, suggesting that thermal nitrogen fixation is insignificant in this reactor. Experimentally, it was also determined that thermal NO was negligible for this system (Wendt et al., 1978). Predictions were also examined to determine the rela-

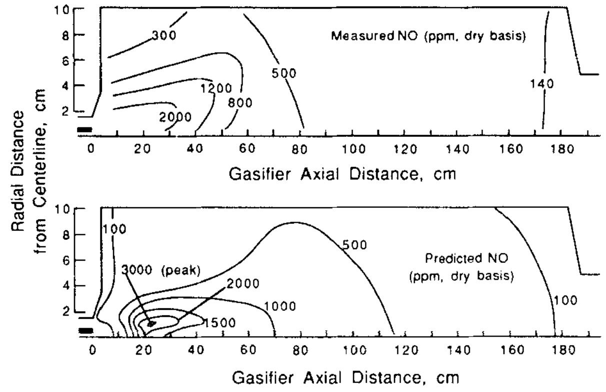

Figure 1. NO concentrations during atmospheric gasification of Utah bituminous coal.
Measured data of Brown (1986)

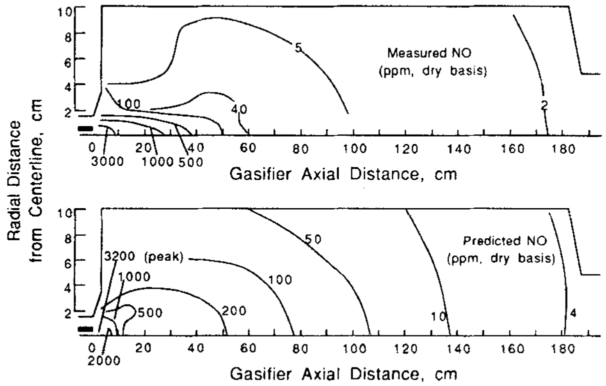

Figure 2. NO concentrations during pressurized (5 atm) gasification of Utah bituminous coal.
Measured data of Nichols et al. (1987)

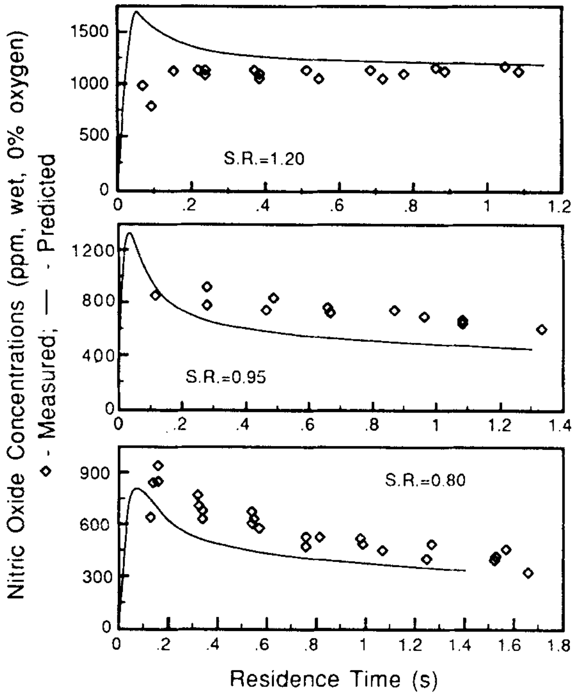

Figure 3. NO centerline profiles for three reactor stoichiometric ratios.
◇ measured (Wendt et al., 1978); — predicted

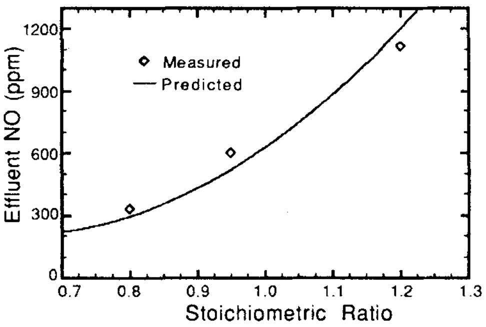

Figure 4. Effluent NO concentrations for various reactor stoichiometric ratios.
Measured data of Wendt et al. (1978).

tive difference between homogeneous and heterogeneous NO reduction. In most fuel-rich locations, where concentrations of HCN were appreciable, the heterogeneous decay was found to be insignificant compared to the magnitude of homogeneous NO decay. This result is consistent with the experimental observation (Dannecker and Wendt, 1984) that gas-phase destruction of NO is the dominant NO reduction path in fuel-rich coal combustion.

Air-Staged Combustion

Staged combustion cases were accomplished by injecting additional air downstream from the fuel-rich primary zones. Two simulations each were completed for primary zone SR values of 0.95 and 0.80. The secondary-zone air was injected at axial locations corresponding to residence times of 0.52 and 0.90 s, bringing the overall reactor SR to 1.20. It was observed that second-stage NO concentrations were independent of primary zone NO levels (Wendt et al., 1978); however, effluent NO concentrations were decreased as the first stage was lengthened because of the fast rate of NO decline in the fuel-rich, high-temperature primary zone. Figure 5 shows the incremental reduction in NO at the exit for both primary-zone stoichiometric ratios. A difference of ~200 ppm NO was measured between the secondary air stage locations of 0.52 and 0.90 s for each case. The predicted difference in NO concentration at the exit closely matches the measured trend.

CO_2-O_2 Oxidizer

A study was recently made to determine the feasibility of producing CO_2 for enhanced oil recovery from combustion of pulverized coal in mixtures of CO_2-O_2 (Berry et al., 1986). Three cases of pulverized coal combustion in different ratios of CO_2-O_2 oxidizer were compared to an air-combustion case of similar feed rate and heat release. On a common gas volume basis, measured NO concentrations first modestly increase and then decrease as shown in Figure 6. The predictions show little change with CO_2-O_2 mixtures, suggesting that substitution of N_2 with CO_2 in the air would have little impact on fuel-NO concentrations beyond dilution effects. The difference of predicted NO and measured NO is less than 2% for the air-combustion case, while an average of 20% difference was calculated for the three CO_2-O_2 oxidizer ratios.

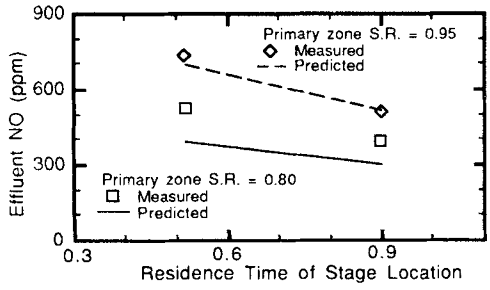

Figure 5. Effluent NO concentrations for air-staged combustion.
Air-stage locations: 0.52 s, 0.90 s. Measured data of Wendt et al. (1978)

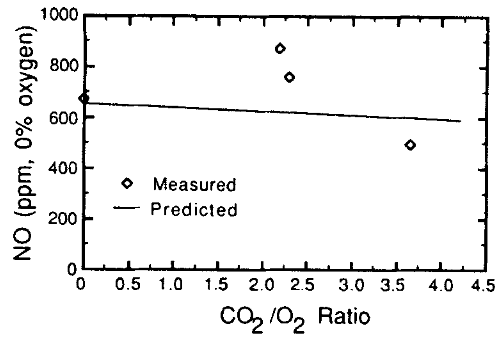

Figure 6. Effluent NO concentrations for combustion of pulverized Colorado bituminous coal.
Measured data of Berry et al. (1986)

Temperature Dependence

From data of fuel-lean (15% excess air) pulverized-coal diffusion flames, fuel NO was observed to be essentially constant over a temperature range up to 2,550 K (Pershing and Wendt, 1977). The NO model predicted similar temperature insensitivity for diffusion-type, fuel-lean (15% excess air) pulverized coal combustion, Figure 7. The weak dependence of fuel NO on temperature in fuel-lean regions is due to similarities in fuel nitrogen evolution for moderate heating rate conditions for a wide variety of coals (Freihaut et al., 1987; Blair and Wendt, 1981). In fuel-rich environments, the influence of flame temperature on fuel NO is greater. NO decay can be accelerated by char/NO and fuel-rich species interactions occurring at increased temperature.

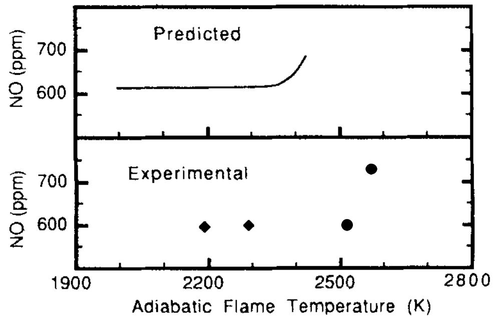

Figure 7. Temperature insensitivity of effluent NO concentrations for fuel-lean combustion of Colorado bituminous coal.
Measured data of Pershing and Wendt (1977); SR = 1.15 Test conditions for predicted and measured cases differed

Acknowledgment

Financial support for this effort has come from a consortium of nine organizations: Babcock and Wilcox, Combustion Engineering, Consolidation Coal Co., Electric Power and Research Institute, Empire State Electric Energy Research Co., Foster Wheeler, Tennessee Valley Authority, U.S. DOE/PETC, Utah Power and Light Company.

Literature Cited

Azuhata, S., P. O. Hedman, L. D. Smoot, and W. A. Sowa, "Effects of Flame Type and Pressure on Entrained Coal Gasification," *Fuel,* **65,** 1511 (1986).

Berry, G. F., C. S. Wang, K. C. Chang, A. M. Wolsky, and U. C. Choi, "A Modeling Study of Pulverized Coal Combustion in CO_2/O_2 Atmospheres," ANL/CNSV-51 (1986).

Boardman, R. D., "Further Evaluation of a Predictive Model for Nitric Oxide Formation During Pulverized Coal Combustion," Master's Thesis, Dept. Chem. Eng., Brigham Young Univ. (1987).

Blair, D. W., and J. O. L. Wendt, "Formation of NO_x and Other Products from Chemically Bound Nitrogen in Coal Combustion," DOE. Final Report DOE/ET/11314-T1 (1981).

Brown, B. W., L. D. Smoot, and P. O. Hedman "Effects of Coal Type on Entrained Gasification," *Fuel,* **65,** 673 (1986).

Dannecker, K. M., and J. O. L. Wendt, "Fuel Nitrogen Mechanism during the Fuel-Rich Combustion of Pulverized Coal," AIChE Meeting, San Francisco (1984).

de Soëte, G. G., "Overall Reaction Rates of NO and N_2 from Fuel Nitrogen," *15th Int. Symp. Combustion,* Combustion Inst., Pittsburgh 1093 (1975).

Freihaut, J. D., W. M. Proscia, and D. J. Seery, "Fuel-Bound Nitrogen Evolution During the Devolatilization and Pyrolysis of Coals of Varying Rank," *1987 Joint Symp. Stationary Combustion NOx Control,* New Orleans (Mar., 1987).

Hill, S. C., L. D. Smoot, and P. J. Smith, "Prediction of Nitrogen Oxide Formation in Turbulent Coal Flames," *20th Int. Symp. Combustion,* Combustion Inst., Pittsburgh, 1391 (1984).

Levy, J. M., L. K. Chan, A. F. Sarofim, and J. M. Beér, "NO/Char Reactions at Pulverized Coal Flame Conditions," *18th Int. Symp. Combustion,* Combustion Inst. Pittsburgh, 111 (1981).

Nichols, K. M., P. O. Hedman, L. D. Smoot, "Release and Reactions of Fuel-Nitrogen in a High-Pressure Entrained-Coal Gasifier," *Fuel,* **66,** 1257 (1987).

Pershing, D. W., and J. O. L. Wendt, "Pulverized Coal Combustion: The Influence of Flame Temperature and Coal Composition on Thermal and Fuel NO_x," *16th Int. Symp. Combustion,* Combustion Inst. Pittsburgh, 389 (1977).

Smith, P. J., S. C. Hill, and L. D. Smoot, "Theory for NO Formation in Turbulent Coal Flames," *19th Int. Symp. Combustion,* Combustion Inst., Pittsburgh, 1263 (1982).

Smith, P. J., L. D. Smoot, and S. C. Hill, "Effects of Swirling Flow on Nitrogen Oxide Concentration in Pulverized Coal Combustors," *AIChE J.,* **32,** 1917 (1986).

Smoot, L. D., and P. J. Smith, *Coal Combustion and Gasification,* Plenum, New York (1985).

Wendt, J. O. L., "Fundamental Coal Combustion Mechanisms and Pollutant Formation in Furnaces," *Prog. Energy Combust. Sci.,* **6,** 201 (1980).

Wendt, J. O. L., J. W. Lee, and D. W. Pershing, "Pollutant Control Through Staged Combustion of Pulverized Coal," U.S. Dept. Energy Tech. Prog. Rept. for Jan. 1977–Dec. 1977, FE-1817-4 (1978).

Manuscript received Sept. 10, 1987, and revision received Mar. 17, 1988.