

LIMITS TO NO_x REDUCTION BY NH₃ INJECTION

John H. Pohl
Energy International
Laguna Hills, CA 92653

Shyh-Ching Yang
Energy and Resources Laboratory
Hsinchu, Taiwan

William A. Sowa and James W. Dill
University of California
Irvine, CA 92717

Keywords: NO_x Reduction by NH₃

INTRODUCTION

The process to reduce NO_x by NH₃ was patented by Lyon (1975). The process initially found limited use to control NO_x in oil- and gas-fired boilers in Japan. The process was experimentally investigated by Muzio, et al. (1976) and Lyon (1978). Typically the NO_x reduction cited in small scale studies or practical application was 40-70 percent. Recently, NH₃ injection systems have been installed on a number of incinerators and fluid bed combustors. The measured emission of NO_x from some of these operating combustors is below 10 ppm (d, 3% O₂). These results implied that better reduction could be achieved than had been thought based on previous small scale results and from field trials.

This paper describes experiments and calculations aimed at establishing the maximum NO_x reduction that can be achieved in the absence of mixing limitations and to determine how gas composition, operating parameters, and additives affect the reduction of NO_x and the slip of NH₃.

EXPERIMENTS

Experiments were designed to be controllable, free of mixing constraints and catalytic influence, and capable of investigating the range of operation of commercial systems. The experimental apparatus, Figure 1., delivers gas from analyzed bottles, mixes and meters the flow through rotometers, adds water vapor as desired from a saturated bath, and passes the gases through a quartz coil reactor in a temperature controlled oven. The bottled gases are mixed to represent the range of flue gases to be treated or the gases after treatment. The gases are analyzed before and after the oven using continuous monitors for NO, NO₂, O₂, CO, and CO₂ and an ion specific electrode for NH₃ concentration.

The conditions investigated were (baseline conditions are underlined):

- o residence time: 0.1, 0.2, 0.5, 1.0 seconds
- o temperature: 1061, 1116, 1144, 1172, 1200, 1228, 1255, 1283, and 1311 K
- o NO: 100, 200, 300, 400, 600, 800 ppm
- o CO: 0, 100, 200, 400, 600, 700 ppm

- o H2O: 0, 6 %
- o CO2: 15 %
- o O2: 3 %
- o NH3/NO: 1, 1.5, 2.0, 3.0, 4.0

Calculations were used to interpret and extend the results of the experimental. Calculation were made using the Sandia National Laboratories SENKIN and the extended mechanism of Miller and Bowman (1989). Selected results from the calculations were fit with mathematical expressions. These expressions allow the data to be easily interpolated and possibly to be extended slightly.

RESULTS

The influence of the above conditions on NOx reduction and NH3 slip were determined by experiment and calculations and were compared with previous experimental data. The following conclusions were derived from the range of conditions studied.

Residence Time

Longer residence times generally resulted in slightly increased reduction of NOx and less NH3 slip. However, shorter residence time, occasionally produced slightly greater NOx reductions and the maximum NOx reduction occurs at lower temperatures for shorter residence times.

Temperature

We find an optimum temperature for the reduction of NOx in the range of 1175- 1225 K and the minimum temperature for nearly complete destruction of NH3 to be greater than 1300 K as shown in Figure 2. and in agreement with other literature values. However, our experimental results show much higher reduction of NOx and much greater NH3 slip compared with the measurements of Muzio, et al. (1976). Our results agree with those reported by Lyon (1979) and calculations made using the unaltered Miller and Bowman Mechanism. The differences between our results and those of Muzio, et al. (1976) may result from their injection of aqueous NH4OH solutions instead of gaseous NH3, mixing limitations in their pilot scale combustor compared to our plug flow reactor, temperature gradients in their reactor compared to our constant temperature reactor, and their use of 100 ppm NO compared to our use of 400 ppm.

H2O

The influence of H2O in the range of 0-6 percent was found to be small on NOx reduction and NH3 slip.

CO

Increased concentrations of CO were found to reduce the NOx reduction and create a peak in the NH3 slip as shown in Figure 3. Our results show that increasing CO concentration from 0 to 700 ppm causes a relative small decrease in NOx reduction, where as the results of Teixeira et al. (1991) show a large increase. Conversely, our results show that increasing

the CO concentration from 0 to 100 ppm can result in a four fold increase in NH₃ slip: higher concentrations of CO reduce the NH₃ slip until the slip reaches a low level at 600 ppm CO. The results of Teixeira et al. show low NH₃ slips at all levels of CO. Again, our experimental results agree with calculations obtained from the unaltered Miller and Bowman Mechanism and the difference between our results and those of Teixeira et al. may result from the difference in experimental conditions particularly any imperfect mixing in their experiment.

NO

The fractional NO reduction decreases with decreased levels of initial level of NO concentration below 400 ppm as shown in Figure 4. Conversely, the level of NH₃ slip increases with increased level of initial NO concentration. The influence of initial NO concentration on NO reduction and NH₃ slip agrees with the results of Muzio, et al. (1976) and the results from calculation based on the Miller and Bowman Mechanism.

NH₃/NO

The level of NO reduction increases as the NH₃/NO level increases to 1.7 as shown in Figure 5. The amount of NH₃ slip increases at NH₃/NO ratios greater than 1.0 to 1.5. The results of our experiments agree with those of Teixeira, et al. (1991) and results of calculations made using the Miller and Bowman Mechanism.

Additives

Calculations on the effect of H₂, H₂O₂, and CH₄ additives injected after the NH₃ injection zone were done to determine the effects of these additives on NO_x reduction and NH₃ slip. The results of these calculations shown in Figure 6. are based on the effluent from the NH₃ reaction zone with a concentration of 8 ppm NO and 81 ppm NH₃. The NO reductions reported in Figure 6. is based on the fractional reduction from an original NO concentration of 400 ppm. Therefore, values greater than 0.02 indicate production of NO after the reaction zone. At the temperatures required to reduce NH₃ to 5 ppm, injection of H₂ and H₂O₂ both result in increases in NO concentration.

Calculations predict injection of CH₄ at a temperature 100 K below the NH₃ injection temperature of 1200 K has little effect on NO_x emission while reducing the NH₃ slip to about 5 ppm. Figure 7. experimentally confirms that CH₄ can reduce NH₃ slip, although not to the levels predicted by the calculations.

ACKNOWLEDGMENTS

The work reported in this paper was sponsored by the Energy Resources Laboratories in Hsinchu, Taiwan and managed through Energy International of Laguna Hills, California. The work was performed at University of California at Irvine, California.

REFERENCES

Lyon, R.K., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," U.S. Patent 3,900554 (1975).

Lyon, R.K., "Thermal DeNOx: How it Works", Hydrocarbon Processing, October (1979).

Miller, J.A. and C.T. Bowman, "Mechanisms and Modeling of Nitrogen Chemistry in Combustion", Prog. Energ. Comb. Sci., 15, pp. 287-338 (1989).

Muzio, L.J., J.K. Arand, and D.P. Teixeira, "Gas Phase Decomposition of Nitric Oxide in Combustion Products", Sixteenth Symposium (International) on Combustion, pp. 199-207 (1976).

Teixeira, D.P., L.J. Muzio, and T.A. Montgomery, "Effect of Trace Combustion Species on SNCR Performance", International Conference on Environmental Control of Combustion Processes, Joint Meeting of the American Flame Research Committee and the Japanese Flame Research Committee, Honolulu, HI, October (1991).

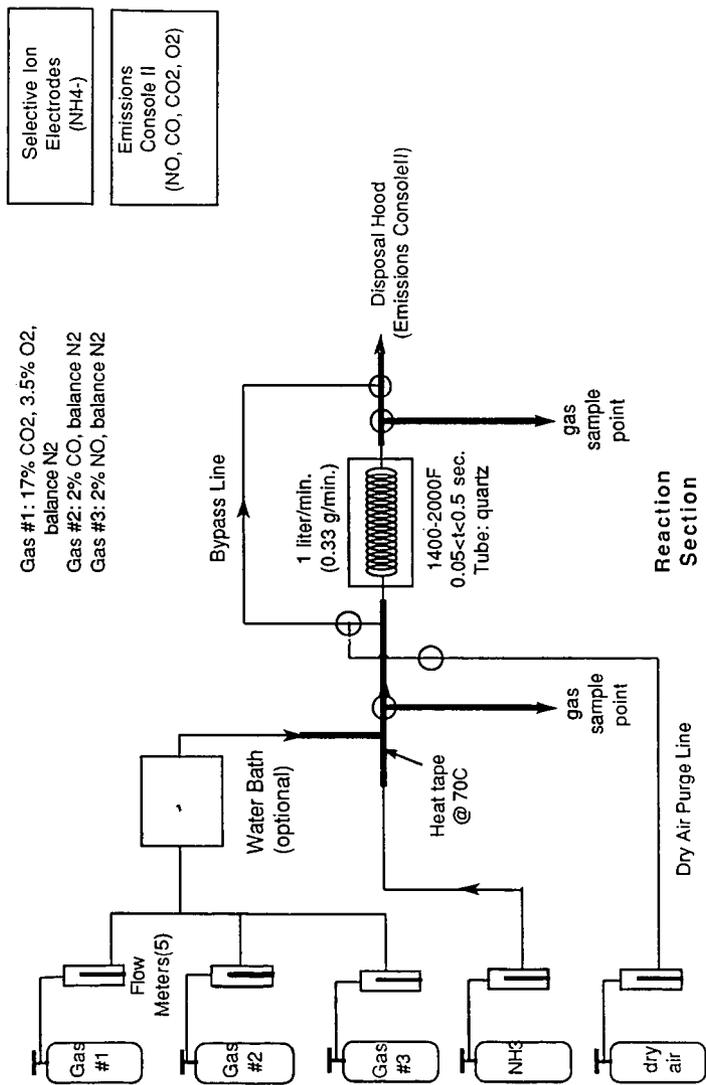
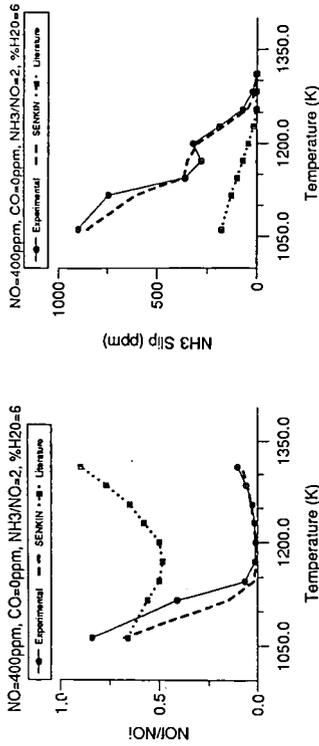


Fig. 1. Experimental Apparatus.

a.) NO Reduction, Experimental Results b.) Residual NH₃, Experimental Results



c.) NO Reduction, Modelled (ppm out/in) d.) Residual NH₃, Modelled (ppm)

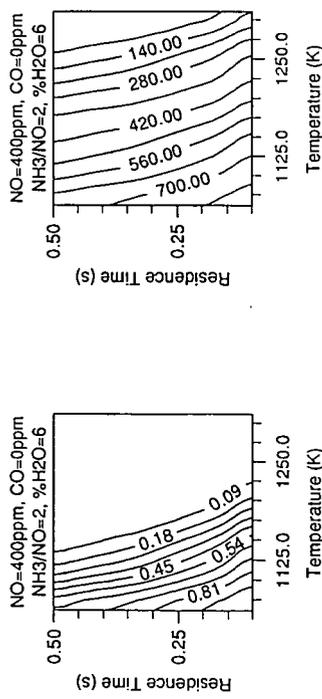
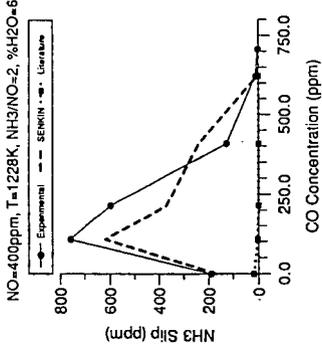
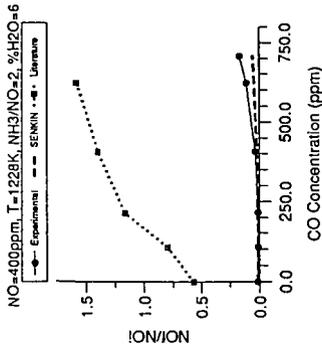


Fig. 2. Effect of Temperature on NO_x Reduction and NH₃ Slip.

a.) NO Reduction, Experimental Results b.) Residual NH₃, Experimental Results



c.) NO Reduction, Modelled (ppm out/in) d.) Residual NH₃, Modelled (ppm)

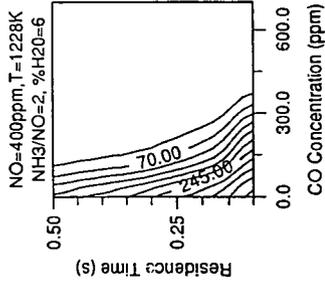
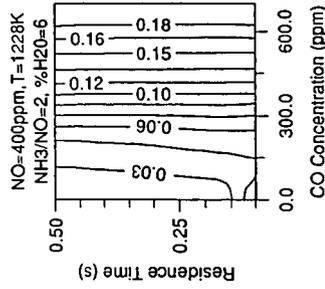
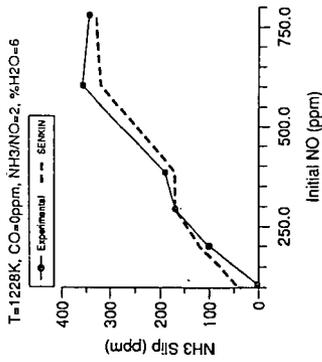
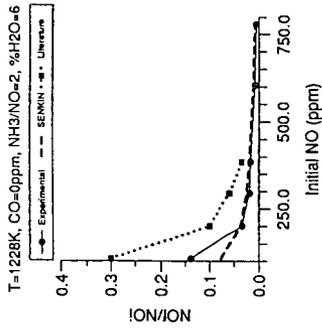


Fig. 3. Effect of CO Concentration on NO_x Reduction and NH₃ Slip. Teixeira, et al. (1991).

a.) NO Reduction, Experimental Results b.) Residual NH₃, Experimental Results



c.) NO Reduction, Modelled (ppm out/in) d.) Residual NH₃, Modelled (ppm)

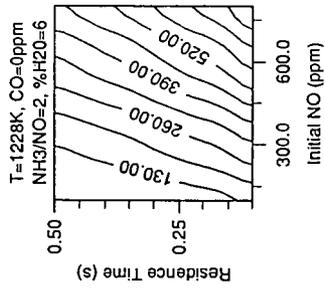
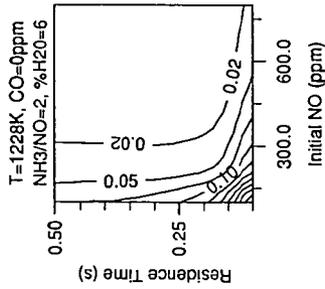
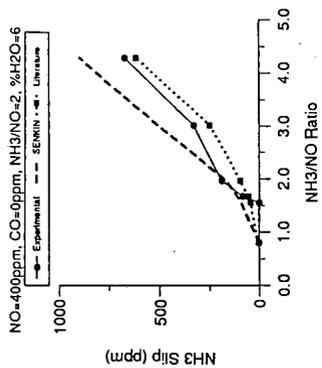
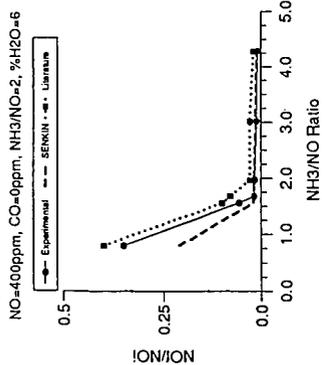


Fig. 4. Effect of Initial NO Concentration on NO_x Reduction and NH₃ Slip. Muzio, et al. (1976).

a.) NO Reduction, Experimental Results b.) Residual NH₃, Experimental Results



c.) NO Reduction, Modelled (ppm out/in) d.) Residual NH₃, Modelled (ppm)

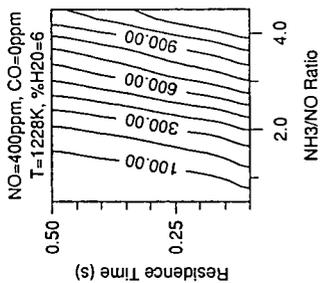
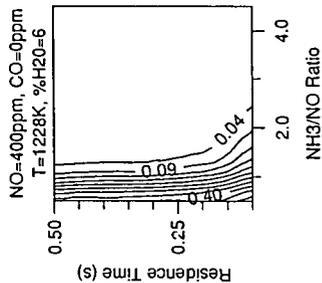


Fig. 5. Effect of NH₃/ NO Ratio on NO_x Reduction and NH₃ Slip. Teixeira, et al. (1991).

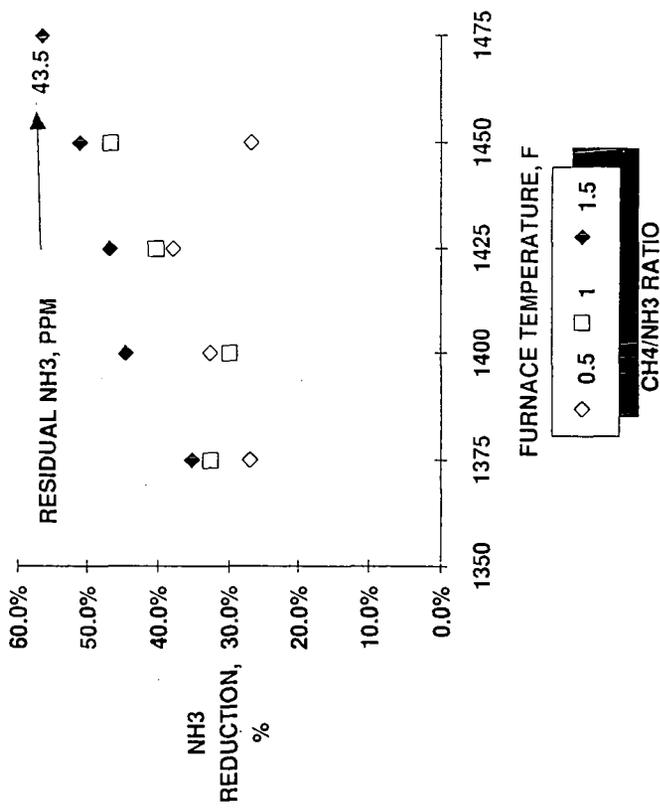


Fig. 6. Effect of CH4 Additive on NH3 Slip.