

Reaction Kinetics of Selective Non-Catalytic
NO_x Reduction with Urea

William H. Sun, Penelope Stamatakis, John E. Hofmann
Nalco Fuel Tech
Naperville, Illinois, U.S.A.

Abstract

Selective Non-Catalytic Reduction (SNCR) of NO_x with urea has proven to be an effective method in controlling NO_x from various stationary combustion sources. The chemistry of this process that is marketed under the name of NO_xOUT®, was modelled to identify major pathways, limitations, and important parameters. The chemical kinetic model includes over 90 elementary radical reactions among various stable and radical species. The developed model has been validated with data generated from a pilot facility.

The model provided understanding of the effects of residence time, treatment rate and baseline NO_x, oxygen and CO concentrations. In addition, the lowest achievable NO_x concentration, referred as 'Critical NO_x', has been identified. This limit is the result of the chemical reaction kinetics. The existence of such limit is explained through reaction chemistry and validated with laboratory and field data.

Introduction

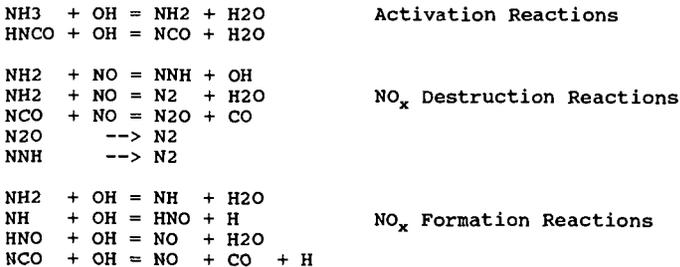
Post combustion NO_x control methods reduce NO_x after its formation is completed. Other methods such as flue gas recirculation and staged combustion limit the formation of NO_x by lowering combustion temperature or by limiting oxygen for N₂ oxidation. Once NO_x is formed, post combustion control methods take advantage of the highly selective reactions between ammonia and NO_x or urea and NO_x. These reactions occur at temperatures between 850 - 1100 °C without a catalyst and are called selective noncatalytic reactions (SNCR). Ammonia injection is an Exxon process and has been called the Thermal DeNO_x Process [1,2] while the urea injection was patented by EPRI [3,4]. Nalco Fuel Tech is EPRI's exclusive licensing agent, and the technology is being marketed as NO_xOUT Process. At lower temperatures (300 - 500 °C), various metal and ceramic catalysts are required to reduce NO_x by reacting with ammonia (SCR)[5].

NO_xOUT Kinetic Model

As part of a development effort, a chemical kinetic model has been developed to understand the basic chemistry, to determine important factors and to define the limits of process capability. This model describes an ideal plug flow, i.e., no temperature or species concentration gradient in radial direction and no back-mixing. Chemical reactions along an ideal plug flow can be described by a set of ordinary differential equations. Reaction rates, density, and thermodynamic information are supplied through a library of

gas-phase subroutines called CHEMKIN developed at the Sandia National Laboratories [6]. The CHEMKIN requires a user supplied chemical reaction set and a thermodynamic data set. The resulting set of equations is integrated simultaneously with a numerical integrator called LSODE [7]. The enthalpy equation is neglected in the model. Instead, measured or calculated temperature profiles are required as an input to the model. Computational fluid dynamics modelling is extensively used to provide temperature and residence time relationships for the kinetic model [8]. Initial conditions are the equilibrium concentrations at flue gas temperatures and excess O₂ as measured. Measured NO_x and CO concentrations are also inputs.

The reaction set is adopted from the work of Miller and Bowman [9]. From this set, reactions involving hydrocarbons were neglected. The wet CO oxidation reactions, ammonia oxidation reactions, and HCN oxidation reactions make up the set. Urea decomposition is modelled as a rapid and one step breakdown to NH₃ and HNCO. The reaction set consists of 92 reactions describing interactions among 31 species. The major pathway of urea breakdown and reaction with NO_x is shown in Fig. 1. Ammonia and HNCO, the assumed breakdown products of urea, must react with chain carrier radicals, O, OH, and H, before reacting with NO. Under oxygen rich conditions, OH concentrations are several orders of magnitude higher than O or H. Therefore, reactions involving OH radicals are more important than those involving O or H. Reaction products of NH₃ and HNCO with OH are NH₂ and NCO. These compounds reduce NO_x or react with OH to form NO_x according to reactions listed below. The balance between formation and destruction of NO_x hinges on concentration of OH and temperature.



Model Validation

Results from a pilot scale combustor are compared with results from the developed model. A schematic of the pilot combustor and the analytical setup is shown in Fig. 2. The test zone of the combustor was kept isothermal by electrical heating. The residence time at this zone was about 0.7 seconds. This is the average residence time between the injection point and the end of the isothermal zone. Urea solution was injected co-flow with an air

atomized nozzle located along the axis of the test zone. Temperature was varied from 700 °C to 1070 °C, baseline NO_x at 300 ppm, and a treatment rate at NSR of 2. NSR is defined as the actual mole ratio of urea to NO_x divided by the theoretical stoichiometric ratio, which is 0.5 for the reaction between urea and NO_x. Comparison of the model and experimental results is shown in Fig. 3. The available chemical reaction time is less than the residence time because part of the residence time is used to distribute and evaporate droplets. Because of these delays, model results for reaction times of 0.1, 0.3, 0.5, and 0.7 seconds are compared to the experimental results. As shown, the trend and the shape of the experimental results are well modelled.

A range of temperature where significant NO_x reductions are obtained is called the temperature window as indicated on Fig. 3. Within this window, controlled NO_x versus temperature curve consists of three zones: left side, right side and plateau. This shape is a result of competing reactions (formation vs. destruction) on the right side and a limitation of reaction time due to slow reaction rates on the left side. On the plateau zone, destruction reaction rates are sufficiently fast while formation reactions are slow, yielding optimum NO_x reductions. Although the reduction is less than the maximum, operation on the right side is practiced and recommended since byproduct emissions are low on the right side [10].

Treatment Rate

Increasing NSR has a diminishing return in NO_x reduction. In Fig. 4, model results of NO_x concentration as a function of NSR are presented at several temperatures. NO_x decreases with increasing NSR at temperatures within the window; increasing NSR increases NO_x at higher temperatures. At temperatures between 900 and 1200 °C, NO_x reaches a limit at an NSR of about 2. A further increase from NSR of 2 increases NO_x for 1200 °C case but has no effect at lower temperatures.

Residence Time

The temperature window becomes wider with an increase in residence time. As shown in Fig. 5, the window is about 150 °C wide at 0.1 second but the window increases to 300 °C at one second. This widening occurs on the left side only and has virtually no effect on the right side. On the plateau region, reactions are essentially complete after 0.6 seconds and even shorter (0.2 seconds) at temperatures above 1100 °C.

Baseline NO_x

The controlled NO_x is unaffected by the baseline NO_x at the plateau zone, while NO_x increased at higher baselines on the left and right sides. Fig. 6 shows NO_x concentration versus temperature at 100, 200, and 500 ppm baseline NO_x. NSR is kept constant at 2 and residence time is 1 second. At 1200 °C, NO_x increased from 100 ppm

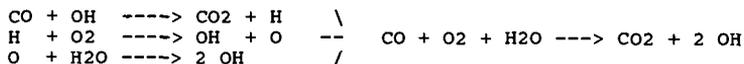
to 120 ppm, but decreased from 500 ppm down to ~300 ppm. This indicates that NO_x can be reduced even at high temperatures provided that baseline NO_x concentrations are also high. In terms of reduction, the temperature window widens toward the higher temperature side with increases in baseline NO_x as shown in Fig. 7.

Excess Oxygen

The effect of excess oxygen is studied by modelling at several levels of excess oxygen and substoichiometric conditions. The fuel equivalence ratio was 1.1 for the substoichiometric case. As shown in Fig. 8, temperature windows are affected slightly as oxygen increased beyond 3%. However, at less than 3% O_2 , the temperature window shifted about 80 °C for a change in excess oxygen from 0.5 to 0.1%. Under a substoichiometric condition, the window shifted to temperatures above 1200 °C. This shift to higher temperatures is the result of reduction in OH concentration. Under a typical oxygen rich condition, OH concentrations are not strongly affected by O_2 . Near the stoichiometric condition, however, a slight decrease in excess oxygen directly reduces OH radicals, which in turn, slows the activation reactions and shifts the window to higher temperatures. Experimental investigation of urea injection under oxygen starved condition by Arand and Muzio also indicates that the window exists at much higher temperature under fuel rich conditions [4]. The present reaction set does not address hydrocarbon reactions and therefore the modelling of stoichiometric and fuel rich conditions needs further work. Nevertheless, very low excess oxygen conditions shift a temperature window to higher temperatures.

Carbon Monoxide Concentration

Carbon monoxide oxidizes to generate H, O, and OH radicals through reactions listed below. Overall, one mole of CO generates two moles of OH radicals.



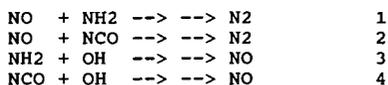
This additional source OH increases rates of the activation reactions and the NO_x formation reactions. A net result is shifting of temperature windows to lower temperatures with CO concentration as shown in Fig. 9. Therefore, CO enhances the process performance when operating on the left side, but degrades reductions on the right side.

Critical NO_x

On Fig. 5, part of the curve that represents the controlled NO_x concentrations at 1 second residence time and at temperatures between 900 and 1300 °C is the lowest achievable NO_x concentration curve. Increases in residence time or NSR do not lower NO_x below this curve. On Fig 10, NO_c concentrations are plotted for the

equilibrium concentration of CO at three baseline NO_x concentrations. At temperatures below 900 °C, 10 seconds of residence time are required to determine the lowest achievable concentration. This minimum achievable NO_x concentration through urea injection, is termed as 'Critical NO_x', as first indicated by Fenimore [11] for the Thermal DeNO_x process. Neither an increase in residence time nor treatment rate above a certain value will lower the controlled NO_x below this critical NO_x concentration.

The existence of critical NO_x and its lack of dependencies to residence time and treatment rate are understood through a simplified chemical kinetic analysis. The change of NO concentration with respect to time for following reactions is formulated as equation 1.



$$\frac{d[\text{NO}]}{dt} = -k_1[\text{NH}_2][\text{NO}] - k_2[\text{NCO}][\text{NO}] + k_3[\text{NH}_2][\text{OH}] + k_4[\text{NCO}][\text{OH}] \quad (1)$$

With urea injection, NO_x concentration will change from its baseline value to a steady state value. At this point, the lefthand side of the above equation becomes zero. After rearranging, an expression for critical NO_x, [NO]_c, is arrived as equation 2.

$$[\text{NO}]_c = \frac{[\text{OH}]\{k_3[\text{NH}_2] + k_4[\text{NCO}]\}}{\{k_1[\text{NH}_2] + k_2[\text{NCO}]\}}; \frac{d[\text{NO}]}{dt} = 0 \quad (2)$$

This equation is further simplified for cases where NH₂ is comparable to NCO, NH₂ is in large excess of NCO, and NCO is in large excess of NH₂.

$$[\text{NO}]_c = [\text{OH}] \frac{(k_3 + k_4)}{(k_1 + k_2)} \quad \text{NH}_2 \sim \text{NCO}$$

$$[\text{NO}]_c = [\text{OH}] \frac{k_3}{k_1} \quad \text{NH}_2 \gg \text{NCO}$$

$$[\text{NO}]_c = [\text{OH}] \frac{k_4}{k_2} \quad \text{NCO} \gg \text{NH}_2$$

These three cases show that NO_c is only a function of OH concentration at a given temperature and does not dependent on residence time or NSR. However, chemicals that generate CO and consequently increase the OH concentration will affect the critical NO_x.

The critical NO_x limits the process on the right side of the window. As shown in Fig. 10, the critical NO_x concentrations are less than 40 ppm at 1050 °C and even lower at temperatures below 1000 °C. These low levels usually do not limit process applications. Instead, the critical NO_x limits achieving low controlled NO_x concentrations at high temperatures where NO_c increases sharply with temperature and baseline NO_x . Finally, reductions are achievable as long as a baseline NO_x is higher than the critical NO_x concentration.

Laboratory and Field Verification

The model study indicates that achievable NO_x concentrations are limited by critical NO_x and this limit is mainly affected by temperatures. Case 1 and case 2 exhibit the process limitation due to NO_c while case 3 shows that reductions are possible even at high temperatures if baseline NO_x is greater than the NO_c .

Case 1.

A NO_x OUT Process testing on a coal fired boiler revealed that NO_x reduction increased with decreasing boiler load, as shown in Fig. 11. At full load, NO_x reduction remained essentially unchanged in spite of a series of injection optimization tests. However, a slight reduction in boiler load from 100% to 90% increased NO_x reduction. At full load, reaction is occurring at the steep part of the NO_c curve, and therefore, NO_x reduction improved rapidly with decreasing load under an essentially identical injection configuration. The controlled NO_x curve on Fig. 10 virtually represents the critical NO_x curve for this boiler.

Case 2.

During a process demonstration at an ethylene cracker, NO_x reduction was limited regardless of the NO_x OUT Process parameters. The cracker unit operated steadily at a temperature of approximately 1050 °C. When the unit operated at a higher NO_x baseline, NO_x reduction increased, but the lowest achievable NO_x concentration remained the same, as shown in Fig. 12. Increasing NSR or other methods to optimize chemical distribution had no effect on the lowest controlled NO_x . This showed the existence of critical NO_x that is unaffected by NSR, chemical distribution, or baseline NO_x .

Case 3.

An increase in NO_x baseline shifts the right side of the temperature window to a higher temperature. To verify this, a pilot scale combustor was operated at 1200 °C and the baseline NO_x concentration was increased from 150 to 750 ppm. At baseline NO_x below about 200 ppm, NO_x increased with urea injection, while at higher than 200 ppm, NO_x decreased as shown in Fig. 13. Comparison with ammonia injection showed that urea is more effective in reducing NO_x at high temperatures than ammonia.

Conclusions

The reaction kinetic model has proven to be a valuable tool in the development of the NO_xOUT Process. Model predictions with respect to the temperature window, the effect of residence time and CO, the effect of very low excess oxygen, and the phenomenon of critical NO_x, which limits NO_x reduction at the high end of the temperature window, have all been verified in laboratory and field tests. The temperature window is defined primarily by residence time at the low temperature (left) side and by baseline and critical NO_x at the high temperature (right) side of the window.

The model is now used to define temperature/residence time requirements for specific applications and to predict maximum achievable NO_x reduction. The model has also shown that the NO_xOUT Process can be applied at higher temperatures than previously thought applicable provided that the NO_x baseline is sufficiently high.

References

1. Lyon, R.K., U.S. Patent 3,900,559, 1975.
2. Lyon, R.K., "Thermal DeNO_x: Controlling Nitrogen Oxides Emissions by a Noncatalytic Process", Environ. Sci. Technol., Vol. 21, No. 3, p.231, 1987.
3. Arand, J.K., and Muzio, L.J., U.S. Patent 4,208,386, 1980.
4. Arand, J.K., Muzio, L.J., Teixeira, D.P., U.S. Patent 4,325,924, 1982.
5. Benson, C.E., Chittick, G.D., and Wilson R.P., Selective Catalytic NO_x Reduction Technology for Cogeneration Plants, Arthur D. Little Report, Prepared for New England Cogeneration Association, November 1988.
6. Kee, R.J., Miller, J.A., Jefferson, T.H., "CHEMKIN: A General Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package", Sandia Laboratories Report #SAND80-8003, Livermore, CA, 1980.
7. Hindmarsh, A.C., "ODEPACK, A Systematized Collection of ODE Solvers", Scientific Computing, R.S. Stepleman et al. (eds.), Vol.1 of IMACS Transactions on Scientific Computation, p.55, North-Holland, Amsterdam, 1983.
8. Sun, W.H., Stamatakis, P., Michels, W.F., Comparato, J.R., Hofmann, J.E., "Selective Non-Catalytic NO_x Control with Urea: Theory and Practice, Progress Update", AFRC 1992 Fall International Symposium, October 1992.
9. Miller, J.A., Bowman, C.T., "Mechanism and Modeling of Nitrogen Chemistry in Combustion", Fall Meeting of the Western States Section/The Combustion Institute, Dana Point, California, October, 1988.
10. Epperly, W.R., O'Leary, J.H., Sullivan, J.C., U.S. Patent 4,780,289, 1988.
11. Fenimore, C.P., "Destruction of NO by NH₃ in Lean Burnt Gas", Combustion and Flame, 37, 245, 1980.

POST COMBUSTION NO_x REDUCTION with UREA

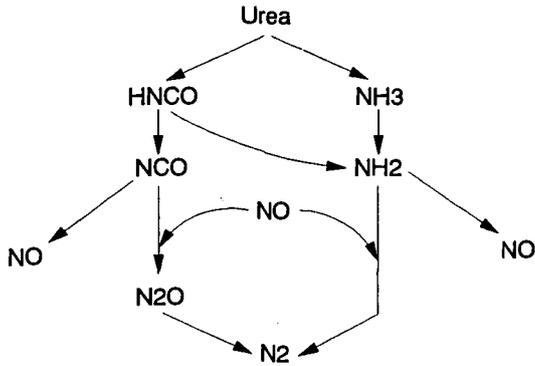


Fig. 1

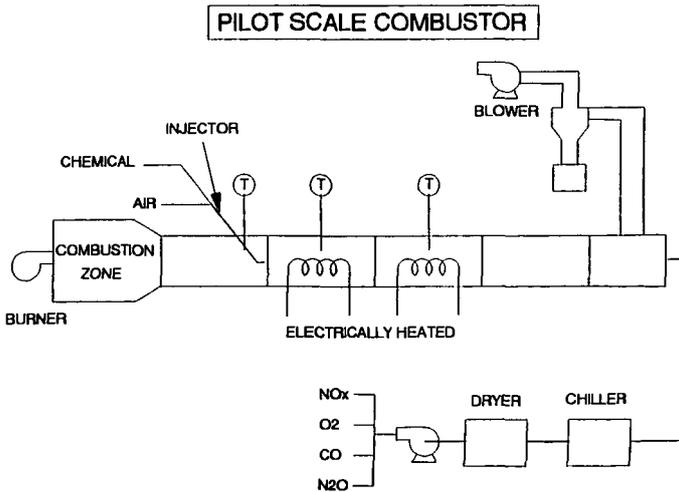


Fig. 2

Effect of Temperature on NOx Reduction

Urea Injection, NSR = 2, NOxI = ~300ppm
Comparison of Model vs. Experimental

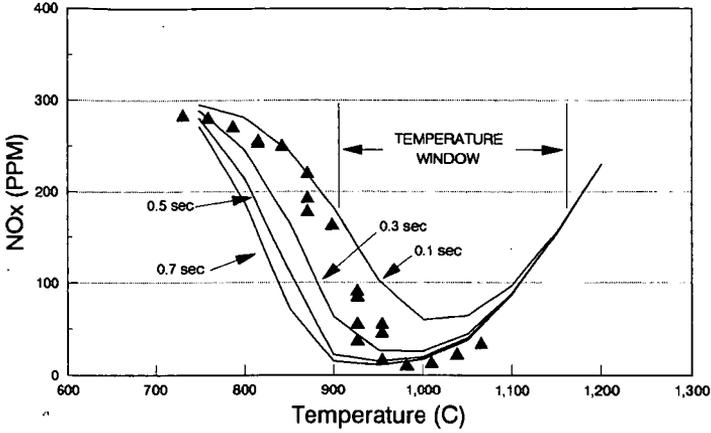


Fig. 3

Effect of NSR on NOx Reduction

Residence Time = 1 sec, NOxI = 200 ppm
NOxOUT Kinetic Model

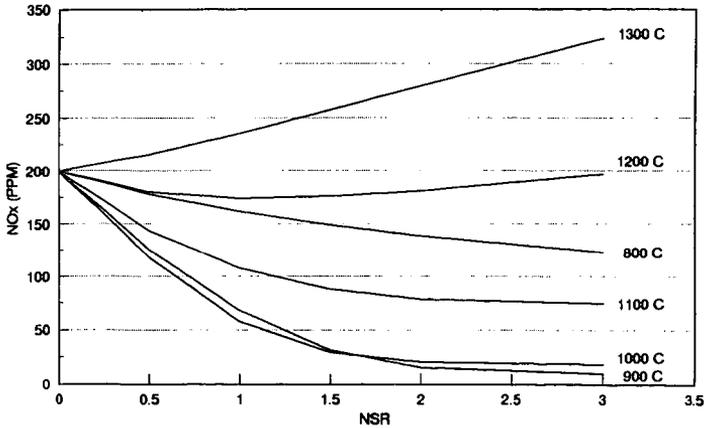


Fig. 4

Effect of Residence Time on NOx Reduction

NSR = 2, NO_xi = 200 ppm
NO_xOUT Kinetic Model

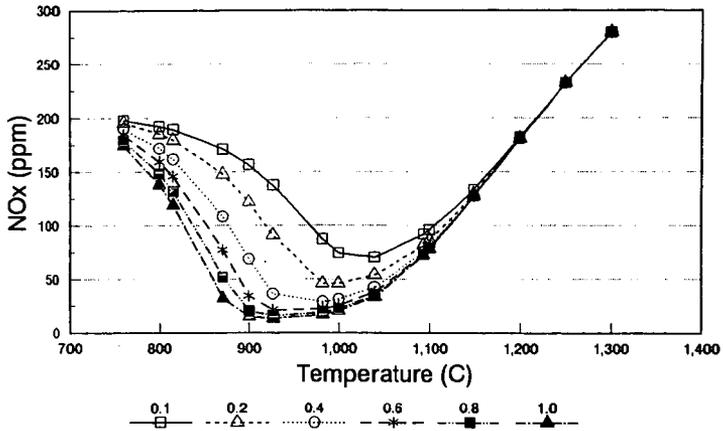


Fig. 5

Effect of Baseline NOx

NSR = 2, O₂ = 3%, Residence Time = 1 sec.
NO_xOUT Kinetic Model

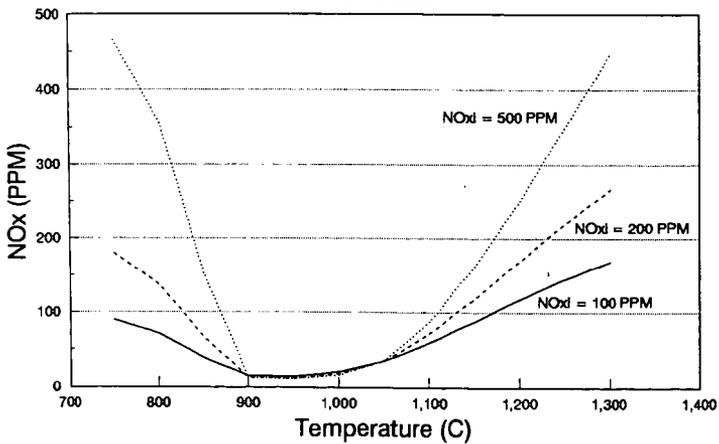


Fig. 6

Effect of Baseline NOx on Temperature Window

NSR = 2, Residence Time = 1 sec.
NOxOUT Kinetic Model

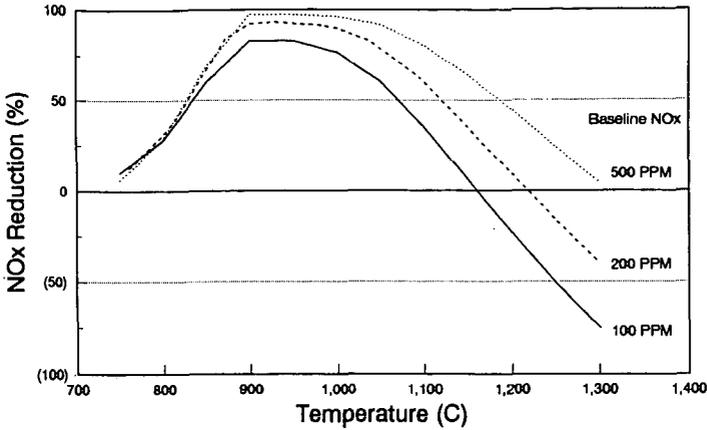


Fig. 7

Effect of O2 Concentration on NOx Reduction

NSR = 2, Residence Time = 1 sec., NOx = 200 ppm
NOxOUT Kinetic Model

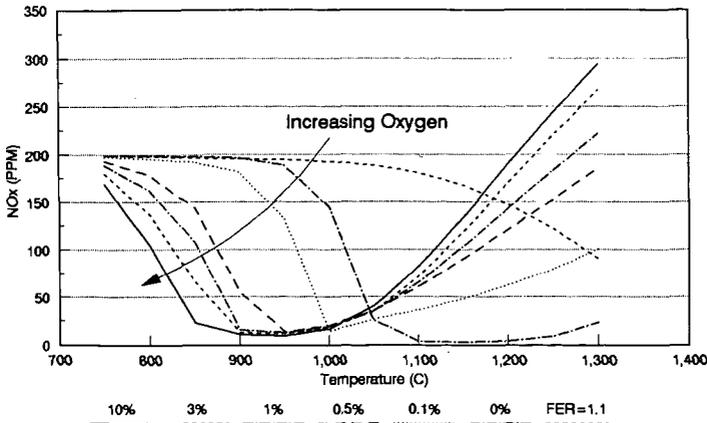


Fig. 8

Effect of CO Concentration on NOx Reduction

NSR = 2, Residence Time = 1 sec., NOxI = 200 ppm
NOxOUT Kinetic Model

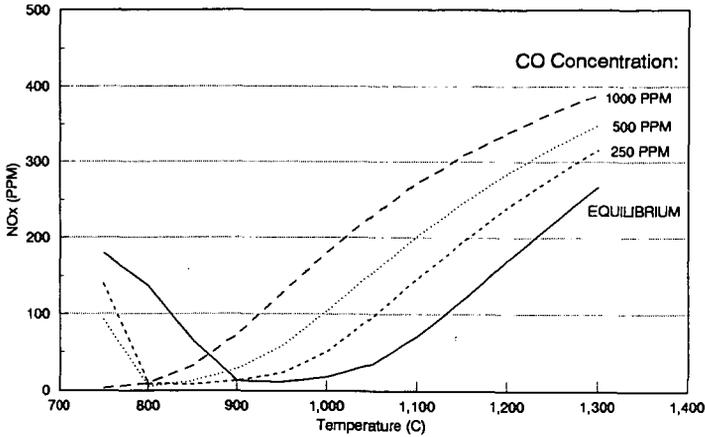


Fig. 9

Critical NOx Concentration

3% Excess Oxygen, Equilibrium CO Concentration
NOxOUT Kinetic Model

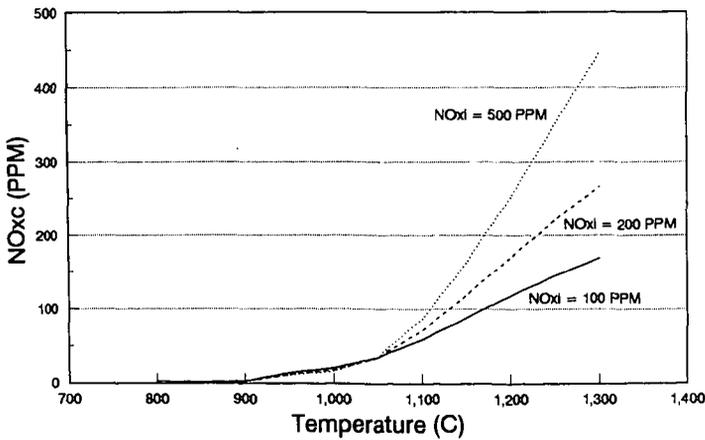


Fig. 10

Effect of Boiler Load on Controlled NOx

NOxOUT Process Testing on a Coal-Fired Boiler

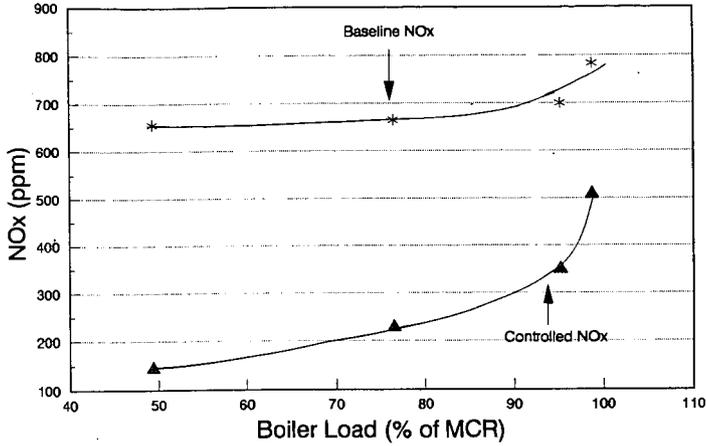


Fig. 11

NOx REDUCTION AT ETHYLENE CRACKER

Temperature - approximately 1050 C

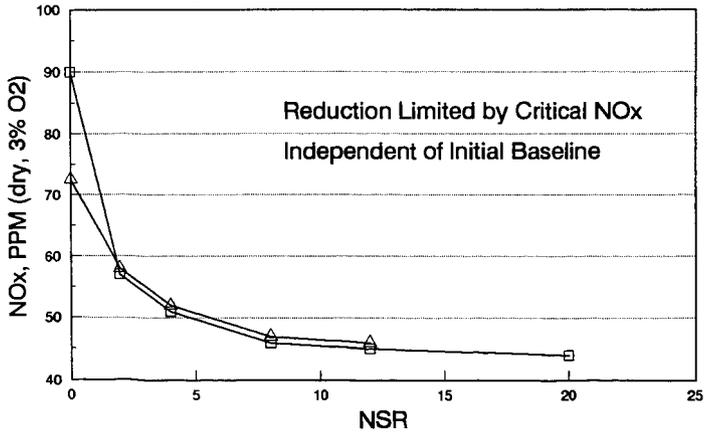


Fig. 12

Effect of Baseline on NOx Reduction

Result from Pilot Scale Combustor, NSR = 2

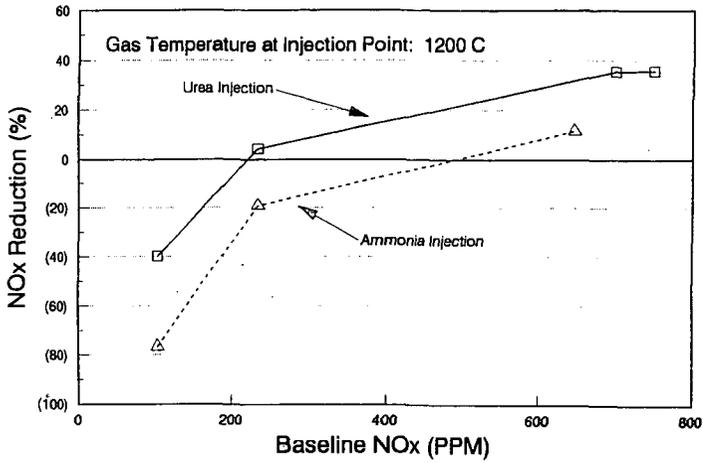


Fig. 13