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ABSTRACT

The formation and destruction of nitrogenous species in the fuel rich coal post flame of a laboratory coal combustor were explored. The fuel rich zones in reburning and air staging configurations were compared under a variety of conditions. The objective was to determine the relative significance of homogeneous and heterogeneous sources of HCN formation and to extract models that can predict nitrogenous species profiles in fuel rich zones.

Heterogeneous effects on HCN formation due to the slow release of nitrogen from the coal residue were of minor significance. HCN formation and destruction in fuel rich regimes were governed by homogeneous gas phase kinetics. The contribution of Fenimore nitrogen fixation reaction to HCN formation limited the destruction of nitrogenous species in fuel rich regimes.

The interconversion of nitrogenous species in the fuel rich pulverized coal post flame could be adequately described by a simplified mechanism based on known fundamental gas phase kinetics with no adjustment of rate coefficients and partial equilibrium assumptions. The proposed model was successful at predicting NO, HCN and NH_3 profiles under reducing conditions in both reburning and staged combustion configurations.

INTRODUCTION

Nitrogen oxides emitted from stationary combustion sources are significant contributors to atmospheric pollution. Fuel rich regimes play important roles in staged combustion of pulverized coal as in air staging and reburning. Most of the destruction of NO takes place in an oxygen deficient environment by allowing a significant fraction of the primary NO to be destroyed to form N_2 or other nitrogenous species.

Air staging is a two stage combustion process in which the primary zone is fuel rich and the air required to complete combustion is added downstream of the primary zone. On the other hand, reburning[1] is a three stage combustion process. A secondary fuel is injected downstream of the fuel lean primary combustion zone, a fuel rich reburn zone is obtained and air is added further downstream to obtain an overall fuel lean environment. Both forms of combustion modification techniques, for NO_x control, have attractive features and are capable of reducing NO emissions by more than 50% depending on various parameters[2,3].

The current study is concerned with the quantification of mechanisms that control the destruction and formation of all nitrogenous species in the fuel rich zone of a coal combustion modification process. Results obtained from reburning studies and air staging studies were used for this purpose. These two forms of NO_x control techniques are different configurations in terms of temperature profiles and local hydrocarbon concentrations. Nevertheless, in this paper we attempt to demonstrate that the kinetic processes that govern the interconversion of nitrogenous species in a fuel rich regime are not strongly dependent on the overall configuration. Consequently, a common mechanism can be used to describe the fate of the nitrogenous species in a reducing environment. The experiments were conducted in a laboratory downflow pulverized coal combustor having temperature and time attributes of practical combustors, but well defined to allow the extraction of mechanisms.

Kremer and Schulz[3] examined NO formation and destruction in the fuel rich staged combustion under nearly isothermal conditions. Their results show that HCN and NH_3 profiles depended on stoichiometric ratio, but not on temperature. Chen et al.[6] conducted a parametric study of 50 different coals to investigate the impact of coal properties on the fate of coal nitrogen. Exhaust NO emissions were correlated with gas phase total fuel nitrogen and char nitrogen. Bose et al.[14] investigated the effects of coal rank on the formation and destruction of nitrogenous species. Heterogeneous processes were found to be important in governing the temporal profiles of nitrogenous species. In a more recent study, Bose and Wendt[7] proposed that NO destruction by hydrocarbon radicals would not influence NO decay except in regions close to the hydrocarbon injection point. NO decay occurred primarily by NO reactions with NH_i radicals and the reduction was first order with respect to NO and NH_3 for all conditions and all coals. Time resolved profiles of HCN in the coal post flame suggested a source of HCN down the combustor since HCN did not decay to correspond to increasing NH_3 concentrations. The researchers hypothesized that heterogeneous release of nitrogen from the coal residue would provide a continuous source of HCN. Fenimore nitrogen fixation reactions were excluded as a significant contributor to HCN formation. Their mechanism successfully predicted NO decay in fuel rich coal flame flue gases and HCN profiles in gas flame flue gases, but failed to account for all nitrogenous species.

A parametric study of reburning was conducted by Chen et al.[4] to investigate the factors which affect the overall effectiveness of reburning. Lanier et al.[5] studied the destruction of NO during reburning in a package boiler simulator and proposed that the formation of HCN by reactions of N_2 with hydrocarbon radicals would limit the effectiveness of reburning.

The previous works mentioned above involved either a reburning or a staging configuration. In this work, fuel rich regimes in both configurations were examined and compared. Furthermore, there is still need for a simple mechanism that can describe the fate of nitrogenous species in fuel rich regimes regardless of the overall configuration. Thus, the following specific issues are addressed: 1) what is the relative significance of homogenous and heterogenous processes in the interconversion of nitrogenous species in fuel rich regimes? 2)to what extent do such mechanisms depend on the overall configuration and coal composition? 3)can a unified simple mechanism describe the fate of nitrogenous species in fuel rich regimes?

EXPERIMENTAL COMBUSTOR

Figure 1 shows a schematic of the 15 cm ID laboratory combustor used in this work. A more detailed description of the combustor is given by Bose et al.[14]. The combustor was later modified (reburning experiments) so that the inner layer of vacuum formed alumina cylinders was replaced by a more durable layer of silicon carbide refractory. The combustor allowed self sustaining combustion of 1-2 kg/h coal, with no external heating, in a configuration that was representative of practical units in terms of characteristic times and temperatures. The unit was designed to bridge the gap between the more fundamental flat flame and drop tube experiments and pilot and full scale coal combustion tests. The burner was designed to produce a premixed flame as described by Bose et al.[14].

In the reburning experiments, the first stage stage was operated fuel lean and natural gas reburn fuel (CO and H_2 for some tests) was injected downstream. The reburn fuel injector was designed to produce adequate mixing in the reburn zone (within 0.18 s). Consequently, temperature and species profiles were independent of radius downstream of the first port below the injection point. The injector tip was supported by a water cooled holder and consisted of 8 holes, 0.14 cm ID each, which allowed the reburn fuel to flow radially with respect to the probe axis. Nitrogen gas was injected with the reburn fuel to produce jet exit velocities that were at least 70 times the bulk flue gas velocity.

The fuel rich staged combustion data discussed in this study (14 runs), were extracted from the work of Bose[13]. These burning tests were conducted under a wide range of conditions, with fuel rich stoichiometries ranged from 0.6 to 0.8. Three different coals were used: Utah Bituminous, German Brown and Texas Lignite. In some experiments, the primary flame was that of natural gas doped with varying amounts of NO and/or NH_3. In many experiments, temperature changes were achieved by N_2 dilution and O_2 enrichment of the primary flame.

Flue gas samples were withdrawn using a water cooled, water quenched probe. The sample was passed through a refrigerated knock out pot and then through in line continuous monitors for O_2, CO, CO_2 and NO_x analysis and also to a gas chromatograph. The chromatograph, outfitted with dual molecular sieve and Porapak T columns and thermal conductivity and flame ionization detectors with argon as carrier gas, was used for H_2, CH_4, C_2H_6 and C_2H_2 analysis. HCN was partly captured by the metered quench water and partly dissolved in 0.1 molar NaOH aqueous solution in a bubbler. After sulfur precipitation, the aqueous samples were analyzed for HCN using an ion specific electrode. NH_3 was captured by the quenched water and analyzed for using a gas specific electrode. The data were then converted to wet ppm values in the flue gas. Temperature measurements were made using an uncoated type R thermocouple, corrected for radiation losses. Residence times were calculated from measured concentrations, corrected temperatures and calculated molar gas rates.

Compositions of the coals that were used for the primary flame in all the experiments discussed in this study are given by Bose et al.[14].

RESULTS

Reburning experiments were conducted under various conditions with reburn zone stoichiometric ratios ranging from 0.68 to 0.9. The emphasis was on natural gas reburning. The primary fuel was either Bituminous coal or natural gas doped with NH_3. For some experiments, non hydrocarbon reburn fuels (CO and H_2) were used to investigate heterogeneous effects on nitrogenous species formation in the reburn zone. The experimental data are presented as time resolved measurements of species and temperatures in the fuel rich zone. As mentioned earlier, the results of 14 staged combustion experiments were selected from the work of Bose[13]. The selection was intended to cover a wide range of stoichiometries and temperatures and involved four different primary fuels.

The profiles shown on figure 2 are typical of fuel rich regimes in air staging and reburning configurations. Time zero was that at the entrance to the fuel rich zone. Fuel rich zone temperatures are usually lower in a reburning configuration than those in a staging configuration. Furthermore, the reburn zone is characterized by high hydrocarbon concentrations, in contrast to the fuel rich zone in staging and most of the interconversion of nitrogenous species occurs within short time scales (less than 0.5 s). The difference that is observed in HCN profiles is possibly due to differences in temperature regimes and hydrocarbon concentrations as will be discussed later.

Reburn zone profiles in which non hydrocarbon reburn fuels (CO and H_2) were used are shown on figure 3. In both cases, CH_4 concentrations in the reburn zone were low (less than 100 ppm) and little NO destruction was observed in both cases. This demonstrates the significance of hydrocarbons in achieving significant destruction of NO. Furthermore, Measured HCN concentrations were less than 7 ppm and measured NH_3 concentrations were less than 16 ppm. This suggests that the release of nitrogen from the coal residue is a minor contributor to HCN formation. This is in contrast to previous observations[7] suggesting that heterogeneous effects might play a critical role in supplying the HCN in the far post flame.

Another source of HCN formation is Fenimore[12] N_2 fixation reactions. The significance of these reactions is not yet clear. Lanier et al.[5] proposed that these reactions would limit the effectiveness of reburning due to the formation of HCN. Subsequent work by Bose[13], showed that such contribution was of minor significance. Figure 4 shows reburn zone profiles for two experiments in which the primary fuel was natural gas. Low primary NO level were measured (24 ppm and 33 ppm). The purpose of these experiments was to minimize HCN formation due to NO destruction by hydrocarbon radicals. In both cases, HCN levels were relatively high (exceeding 40 ppm) resulting in an increase in total fuel nitrogen (TFN = NO + HCN + NH_3) concentrations relative to the primary levels. This is a clear indication that Fenimore N_2 fixation produces HCN, mainly due to $CH + N_2 \longrightarrow HCN + N$, which increases the fixed nitrogen species pool and depletes the hydrocarbon radical pool. This reaction would limit the effectiveness of combustion modification techniques involving fuel rich regimes in reducing NO emissions, especially as NO levels decrease.

The symbols on figure 5 are the results of reburning tests with two different reburn zone entrance temperatures, 1485 and 1657 K, noted as low and high temperature tests, respectively. The curves on figure 5 are predictions based on a mechanism that is discussed later. The low temperature test is more typical of reburn zone profiles with NO decaying over long time scales (0.5 s) and HCN becoming the dominant volatile nitrogenous species. In all cases, NH_3 levels increased with residence time in the reburn zone and then leveled off. NO decay rate was lower at lower temperatures in the reburn zone. On the other hand, both NO and HCN decayed in the high temperature test with HCN concentrations decaying to negligible levels within 0.5 s. This decay corresponded to decay in measured CH_4 concentrations suggesting a correspondence between the trends of HCN and those of methane that is not limited to short residence times. High temperatures in the reburn zone (above 1650 K) are not typical, but may be necessary if low levels of HCN are desired in the reburn zone. Similar trends of HCN decay were observed at comparative temperatures in the fuel rich staged data of Bose and Wendt[7] (also see figure 2).

Figure 6 shows nitrogenous species profiles in the fuel rich zone of a staging configuration for three different coals. For lignite coals (German Brown and Beulah), NH_3 concentrations were higher than those of HCN. The opposite was true for bituminous coal (Utah). This is in agreement with the data of Chen et al.[6]. The curves shown on figure 6 are predictions based on a model that is discussed in the following section.

DATA ANALYSIS

The work of Glarborg et al.[8] was used as a basis for identifying the reactions that were likely to be important. The values of the kinetic rate coefficients, updated by Miller and Bowman[15], were used. No adjustment of any rate constant was made and the analysis was done only in terms of known detailed kinetic mechanisms taken from the literature.

The destruction of NO was based on the reactions:

$$NO + NH_i \longrightarrow products \qquad i = 0,1,2 \tag{1}$$

$$NO + CH_i \longrightarrow products \qquad i = 0,1,2 \tag{2}$$

Partial equilibrium assumptions

$$NH_i + OH = NH_{i-1} + H_2O \qquad i = 1,2,3$$

$$CH_i + OH = CH_{i-1} + H_2O \qquad i = 1,2,3,4$$

were used to calculate NH_i and CH_i concentrations. This yielded the following expression for NO decay:

$$\frac{d(NO)}{dt} = -(NO)(NH_3)f_1 - (NO)(CH_4)f_2 \tag{3}$$

Functions f_i, depending on temperature, OH and H_2O concentrations, are groupings of known elementary reaction rate constants and equilibrium constants.

HCN destruction rate was based on HCN + O reactions, HCN + OH reactions and the reversible reaction $HCN + H \rightleftharpoons CN + H_2$. Pseudo steady state assumption was made for CN and partial equilibrium assumption were made for $HCN + OH = CN + H_2O$ and $OH + OH = O + H_2O$. On the other hand, HCN formation rate was based on reaction (2) in addition to the reactions:

$$CH + N_2 \longrightarrow HCN + N \tag{4}$$

$$CH_2 + N \longrightarrow HCN + H + H \tag{5}$$

This yielded the following expression for the rate of change of HCN:

$$\frac{d(HCN)}{dt} = -(HCN)[f_3 + f_4] + (CH_4)[(NO)f_2 + (N_2)f_5 + (NH_3)f_6] \quad (6)$$

N_2 was formed by $NO + NH_2 \longrightarrow N_2 + H_2O$ and $NO + N \longrightarrow N_2 + O$ and destroyed by reaction (4) yielding:

$$\frac{d(N_2)}{dt} = (NO)(NH_3)f_7 - (CH_4)(N_2)f_5 \quad (7)$$

The rate of change of NH_3 was determined from a nitrogen balance:

$$\frac{d(NH_3)}{dt} = -\frac{d(NO)}{dt} - \frac{d(HCN)}{dt} - 2\frac{d(N_2)}{dt} \quad (8)$$

OH decay was based on $OH + H + M \longrightarrow H_2O + M$, with H in partial equilibrium with H_2O and H_2, yielding the following expression for OH decay:

$$\frac{d(OH)}{dt} = -(H_2)f_8 \quad (9)$$

The f_i in Eq. (3, 6, 7 and 9) have the form

$$f_i = \sum_j A_{ij} T^{N_{ij}} \exp(\frac{B_{ij}}{T}) \times \frac{(OH)^{m_{ij}}}{(H_2O)^{l_{ij}}} \quad (10)$$

where values for parameters can be found elsewhere[16]. Equation 9 was used to calculate the initial OH concentration using measured NO decay rates from the gas flame data only and correlating the calculated values as seen on figure 7. The following expressions were obtained:

$$\frac{(OH)_{initial}}{(OH)_{equil}}\Big|_{reburning} = 4.368 \times 10^{-5} \times \exp(17185/T)$$

$$\frac{(OH)_{initial}}{(OH)_{equil}}\Big|_{staging} = 2.697 \times 10^{-3} \times \exp(10260/T)$$

Equilibrium OH concentration was calculated from measured H_2 and H_2O concentrations based on partial equilibrium $2OH + H_2 = 2H_2O$.

Simultaneous solution of equations 3, and 6-9 can give predictions of all nitrogenous species (NO, HCN, and NH_3), independent of their measured values. The initial concentrations were taken at the first measured point in the fuel rich zone.

Comparison between measured (data points) and predicted (lines) profiles are shown on figures 5 and 6. In general, the proposed mechanism was successful at predicting NO, HCN and NH_3 profiles in the fuel rich zone in both reburning (figure 5) and staging (figure 6) configurations.

Comparison between measured and predicted nitrogenous species concentrations for 14 staging runs[13] and 9 reburning runs (natural gas reburning) is shown by the symbols on figure 8. The model was least successful at predicting NH_3 concentrations which was expected since the rate of change of NH_3 was determined from a nitrogen balance.

CONCLUSIONS

In the study of fuel rich regimes in reburning and staging configurations, heterogeneous effects were minor in forming HCN in the far coal post flame. Consequently, the interconversion of nitrogenous species in fuel rich regimes could be adequately described by homogeneous gas phase kinetics. On the other hand, Fenimore[12] N_2 fixation reaction $(CH + N_2)$ contributed to HCN formation. The significance of this contribution depended on local hydrocarbon and NO concentrations. Thus, this reaction can limit the destruction of nitrogenous species in fuel rich regimes.

Hydrocarbons were critical in destroying NO throughout the fuel rich zone. NO reactions with CH_i and NH_i radicals were both essential in describing nitrogenous species interconversion in fuel rich regimes in both reburning and staging configurations.

These results do not completely concur with the previous conclusions of Bose and Wendt[7], specifically, the role of heterogeneous effects on HCN formation and the relative significance of NO destruction by hydrocarbon radicals.

A simple mechanism, based on homogeneous gas phase kinetics, known kinetic parameters and partial equilibrium assumptions, was successful in describing the fate of nitrogenous species in fuel rich regimes in both reburning and staging configurations.

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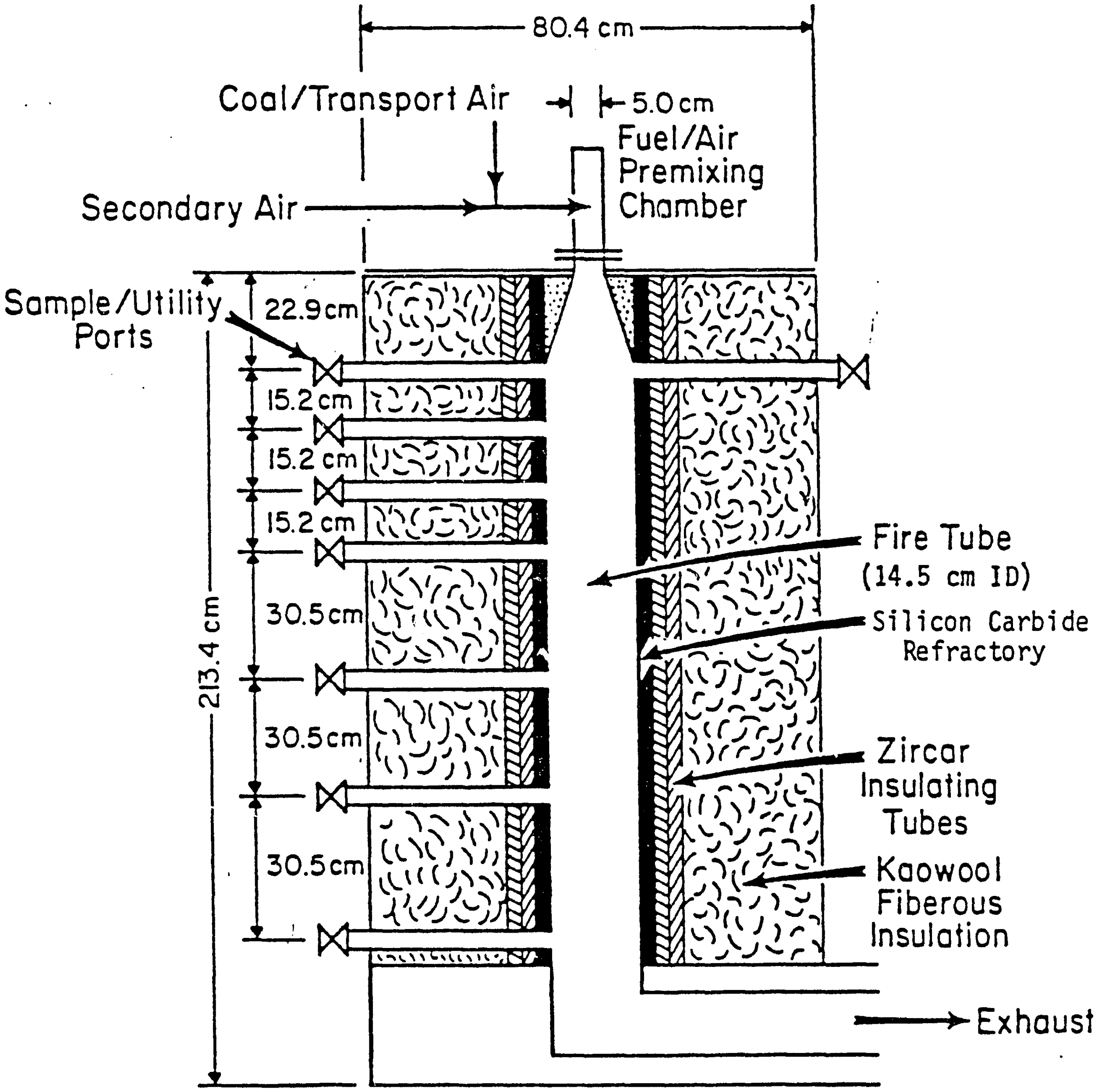

FIG. 1. Experimental Combustor.

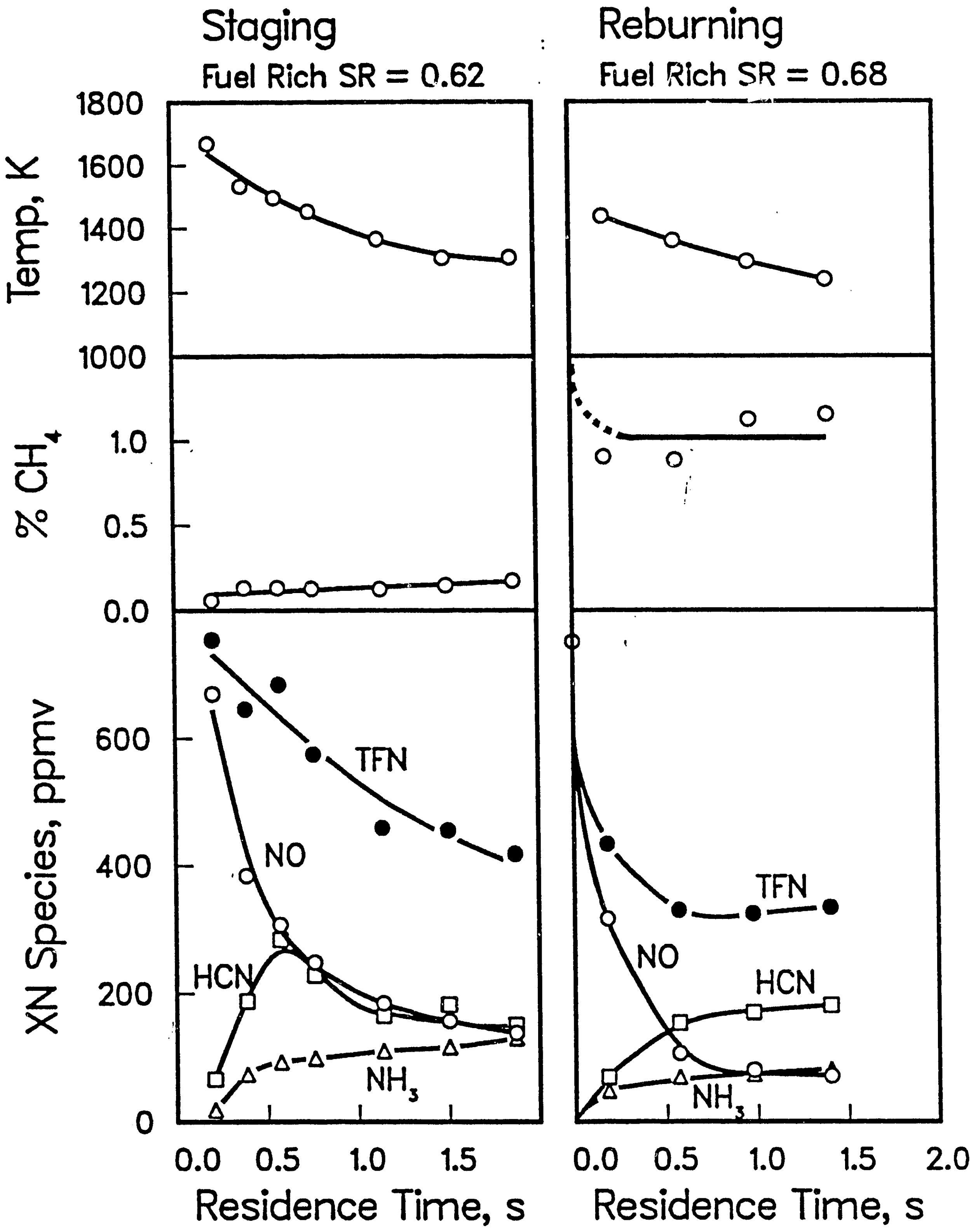

FIG. 2. Typical Fuel Rich Zone Profiles in Staging and Reburning Configurations – Bituminous Coal.

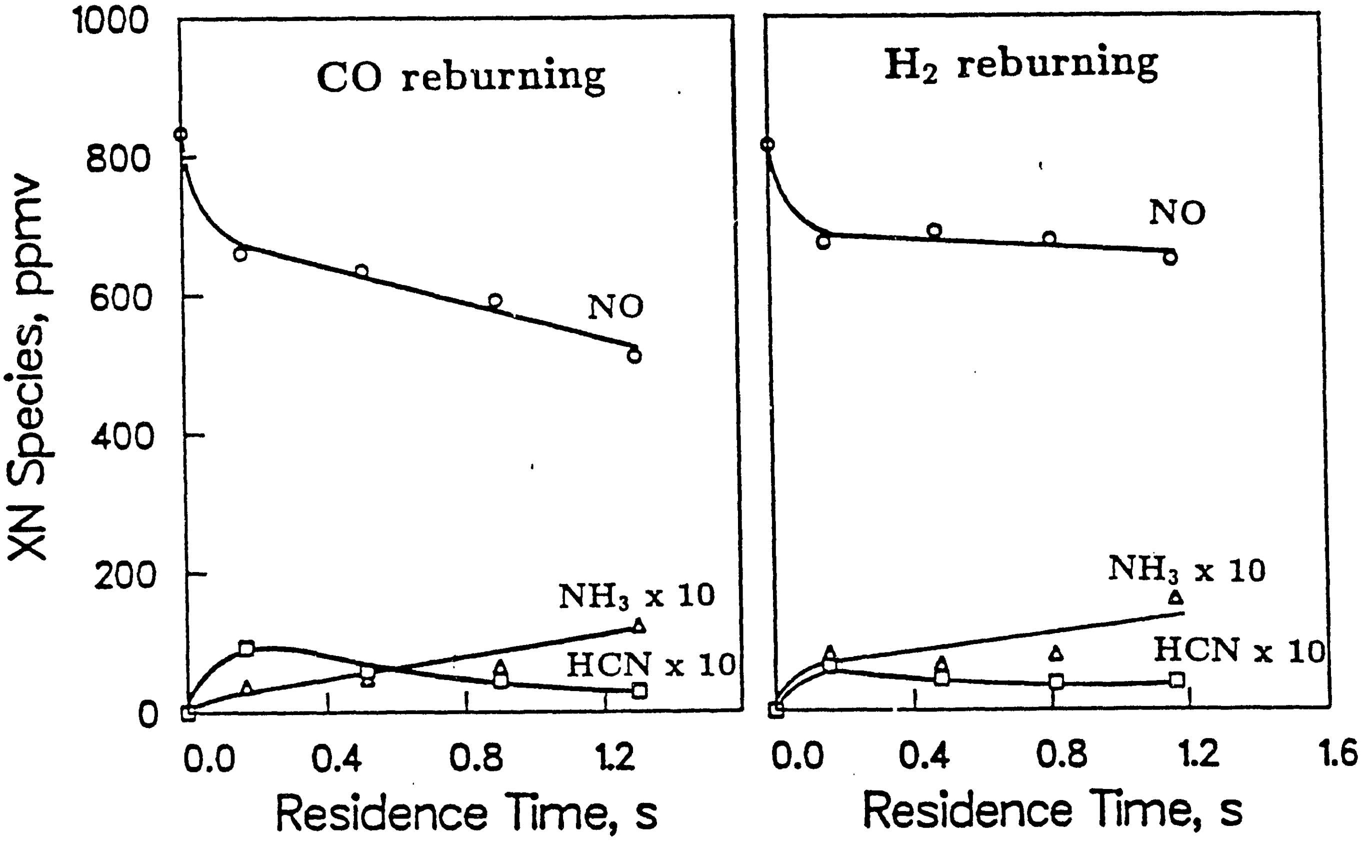

FIG. 3. Fixed Nitrogen Species Profiles in the Reburn Zone – Bituminous Coal Primary Flame and Non-Hydrocarbon Reburning Gas – Fuel Rich SR = 0.90 and $NO_p \approx 825$ ppm.

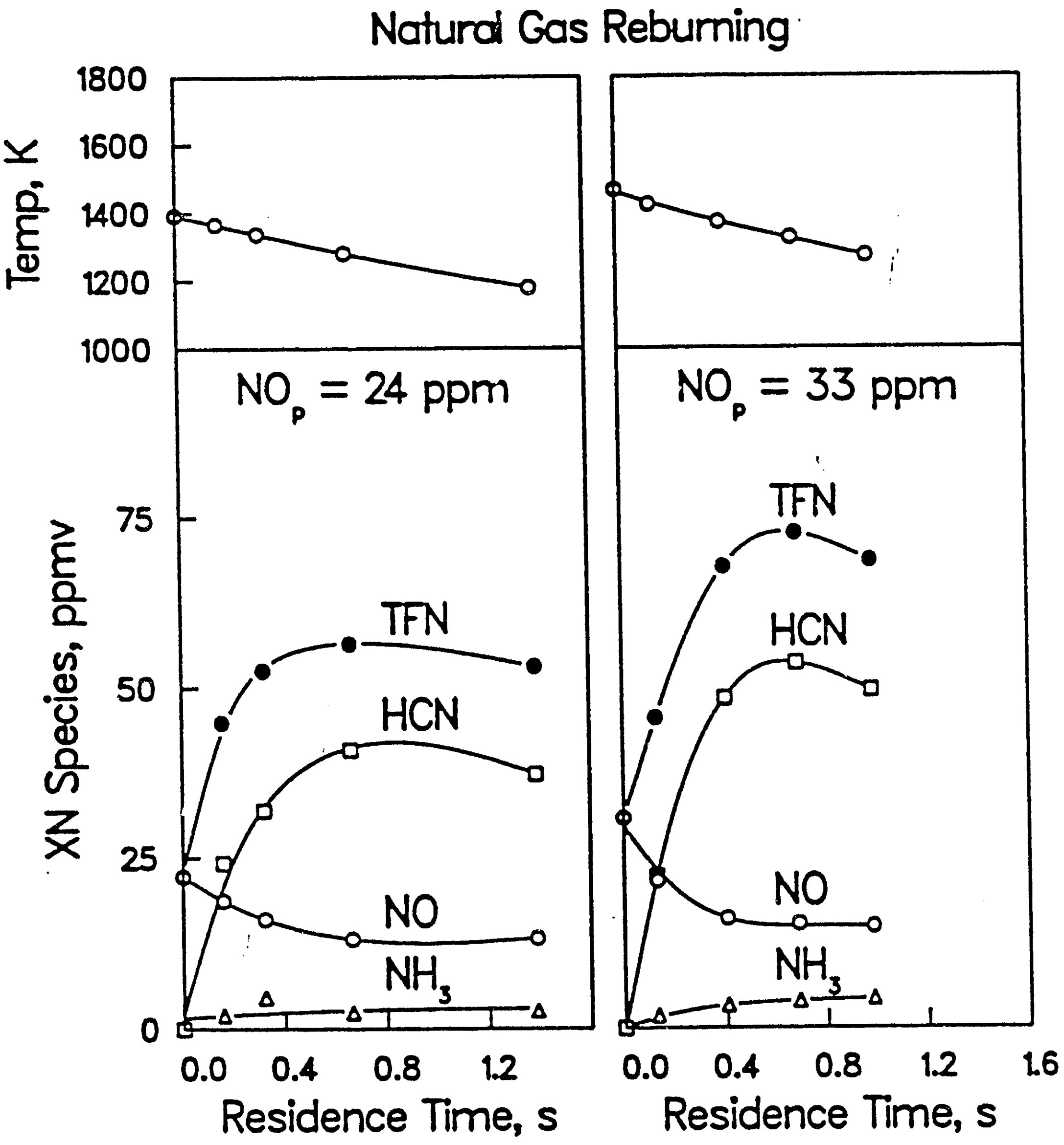

FIG. 4. Reburning at Low Primary NO, SR$_r$ = 0.87.

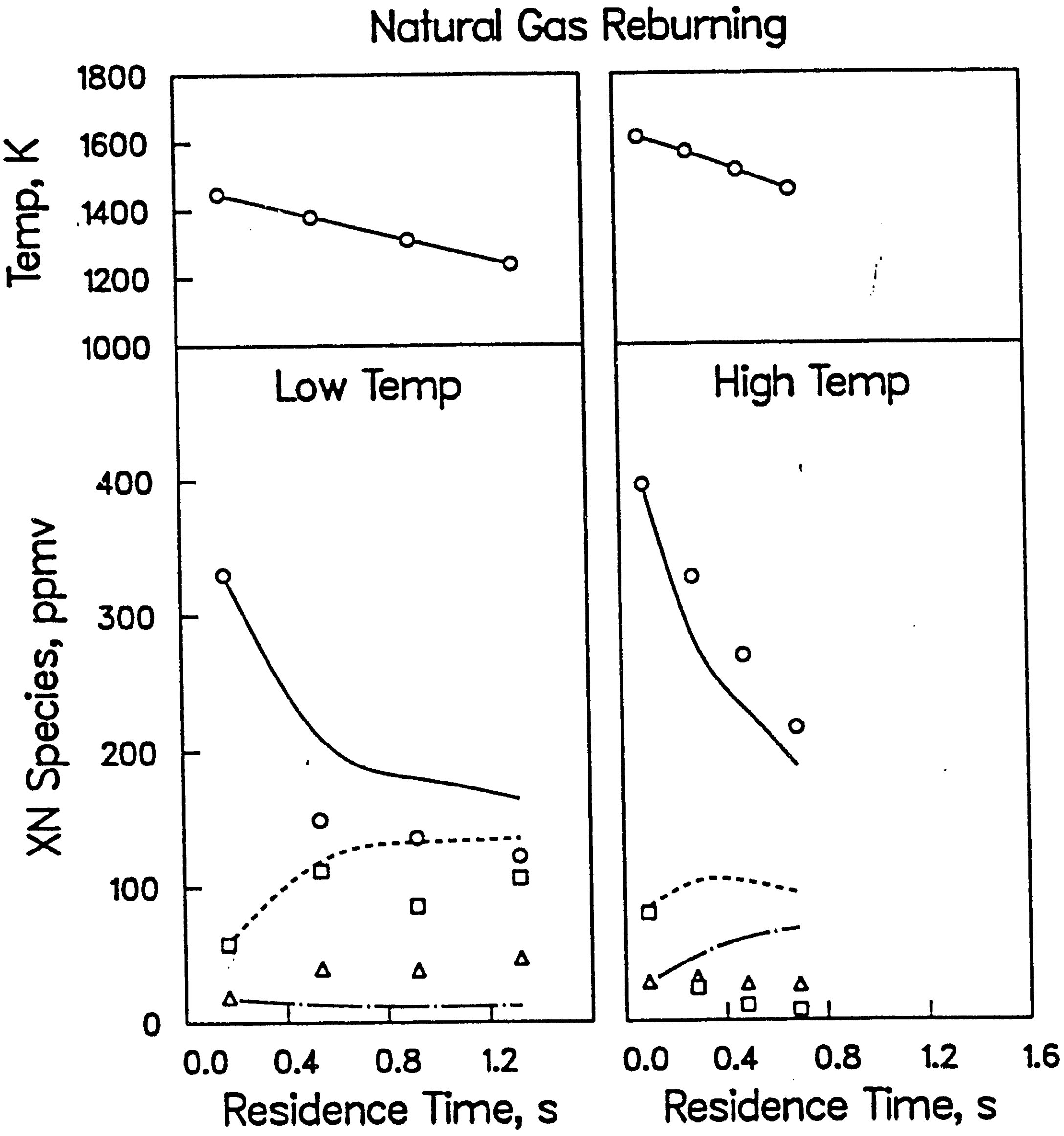

FIG. 5. Fixed Nitrogen Species Profiles in the Reburn Zone – Bituminous Coal Primary Flame – Fuel Rich SR = 0.86.

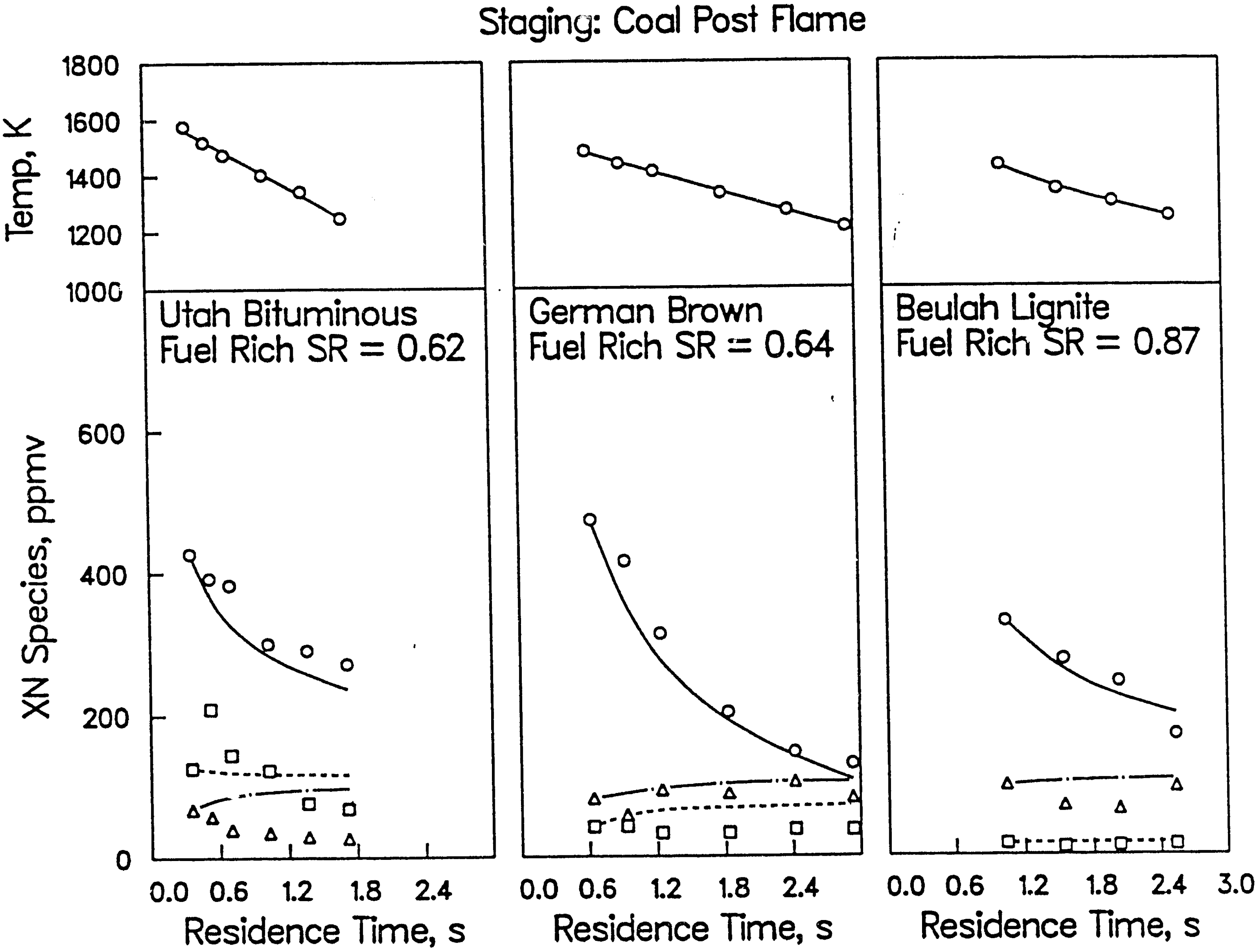

FIG. 6. Fixed Nitrogen Species Profiles in the Fuel Rich Zone – Three Different Coals.

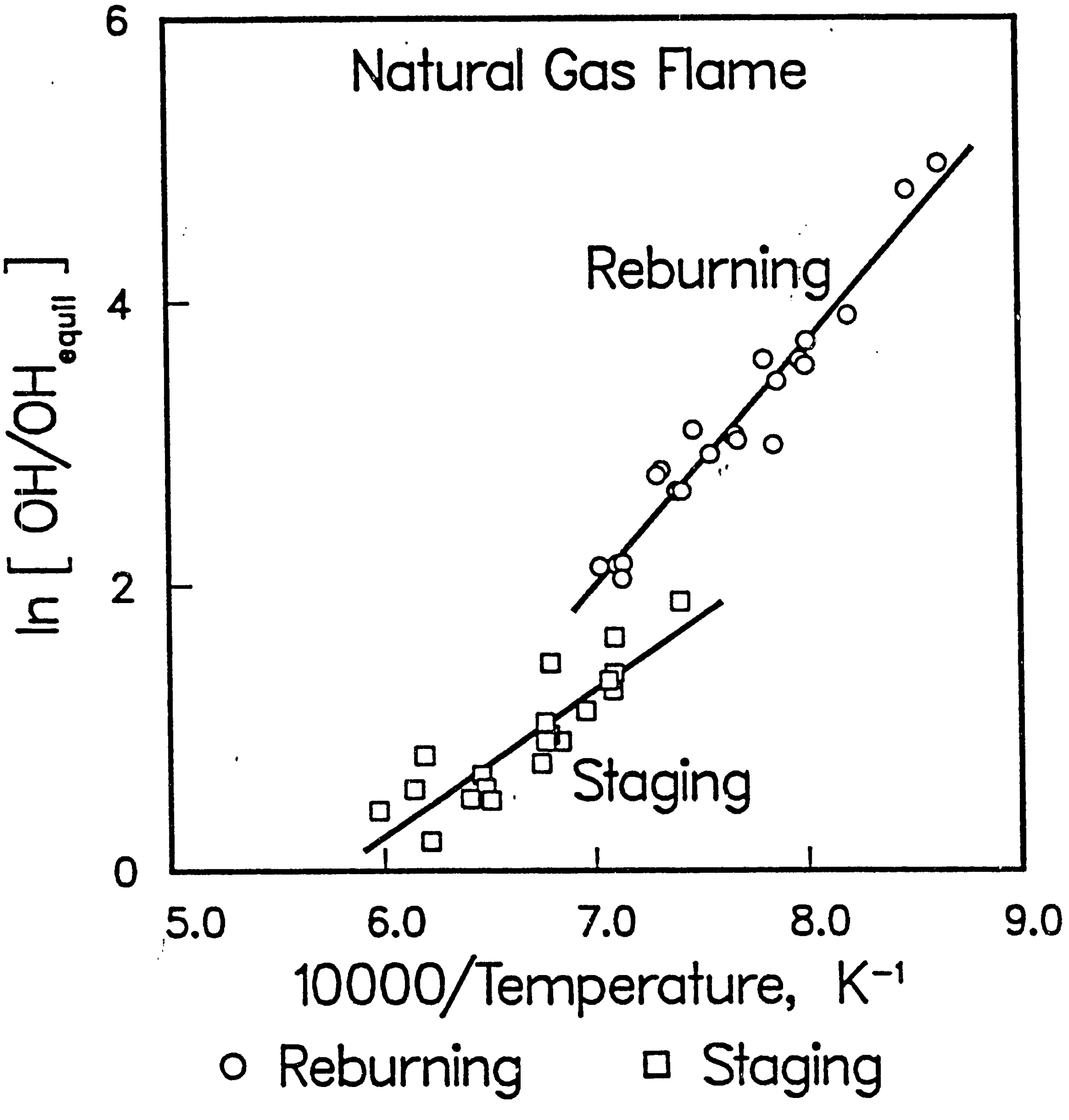

FIG. 7. Hydroxyl Radical Concentration Overshoot under Reducing Conditions.

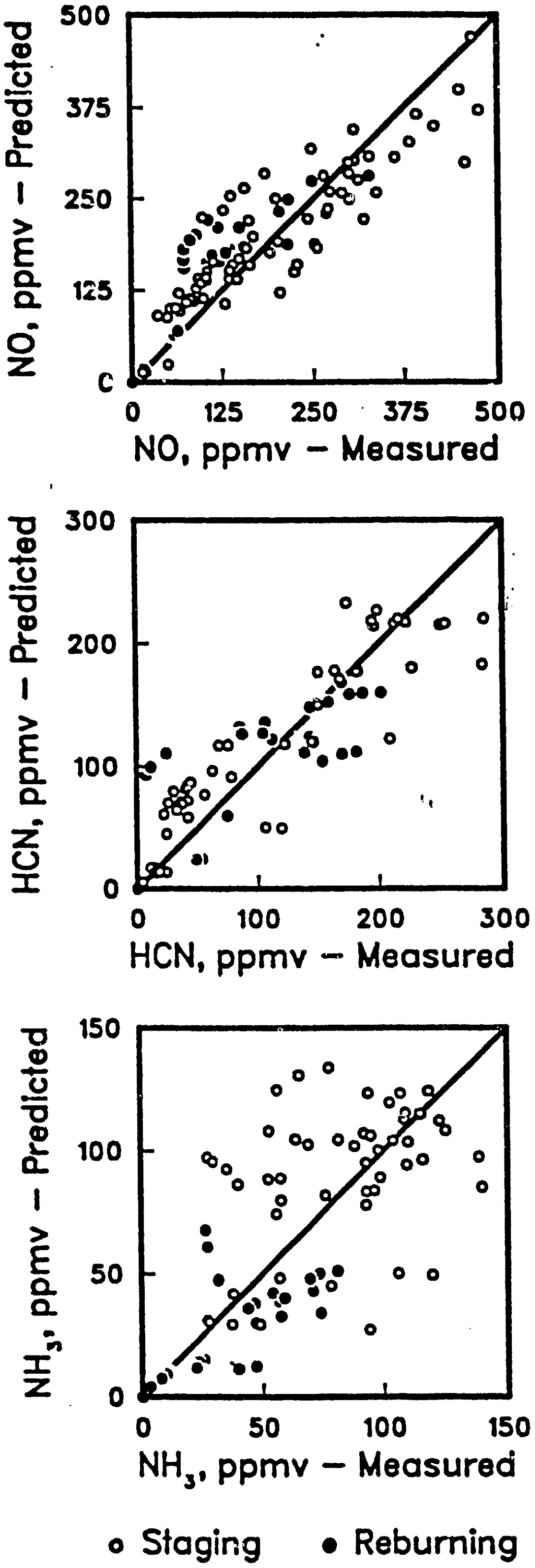

FIG. 8. Comparison between Model Predictions and Measurements.

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