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PULVERIZED COAL COMBUSTION: NO_x FORMATION MECHANISMS UNDER FUEL RICH AND STAGED COMBUSTION CONDITIONS

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A 2 Kg/h pulverized fuel one dimensional flame combustor was used to determine time resolved NO profiles under fuel rich and staged combustion conditions. Seven solid fuels, including two coal chars, were investigated. Results show that at all fuel rich conditions NO is formed rapidly and then is slowly destroyed. The peak NO value and the rate of destruction are strong functions of coal composition and stoichiometry. Under staged combustion conditions NO may increase or decrease at the staging point, depending on the fuel and on the quantity of NO formed in the first stage. Use of artificial oxidants confirmed that under most conditions examined, the NO formed in the first and second stages consisted primarily of Fuel NO.

Heterogeneous formation and reduction of NO during FMC char combustion was modeled by a two-reaction scheme. For this char, heterogeneous reduction was less than first order in NO and had an activation energy of 47 kcal/mole. The roles of devolatilization and homogeneous reactions are discussed, in the light of the data presented.

Introduction

Mechanisms governing the fate of fuel nitrogen during pulverized coal combustion are often controlled by events occurring in a fuel rich environment. This is especially true for staged combustion, which, although known to be effective for NO_x abatement, still requires its optimum configuration to be determined. The focus of this research is to identify experimentally the phenomenological NO_x formation mechanisms that play critical roles under fuel rich and staged pulverized coal combustion conditions and that control the effectiveness of staged combustion for pollutant abatement. Of interest are a) experimental comparison of time-resolved formation and destruction rates of Fuel NO from various pulverized coals, b) determination of global rates of formation and destruction of Char NO and c) the influence of first stage (fuel rich) parameters on the origin and magnitude of "Second Stage (fuel lean) NO."

While previous research[1] established the critical factors influencing exhaust NO emissions from swirling turbulent coal flames, this paper focusses on time resolved measurements of NO under "premixed," one dimensional flow, conditions. We thus attempt to fill the gap between small laboratory scale experiments[2][3] which elucidated the effect of equivalence ratio, particle heating rate and temperature on the evolution of nitrogeneous species during coal pyrolysis and large pilot scale experiments[4] which found that increased residence times at fuel rich conditions led to lower exhaust NO values after staging.

Experimental Combustor

A schematic of the experimental combustor is shown in Fig. 1. In essence, the "premix" burner arrangement pioneered by others[5] was incorporated into a 15 cm ID, 2 Kg/h plane flame combustor system that allowed second stage air to be injected through opposite pairs of sidewall injectors, while still allowing axial profiles of species to be obtained.[6] Combustion of all fuels was self sustaining and radial traverses at various axial positions confirmed[6] the one dimensional nature of the flow. Second stage injectors were so designed to distribute the second stage air rapidly[7] and uniformly in the

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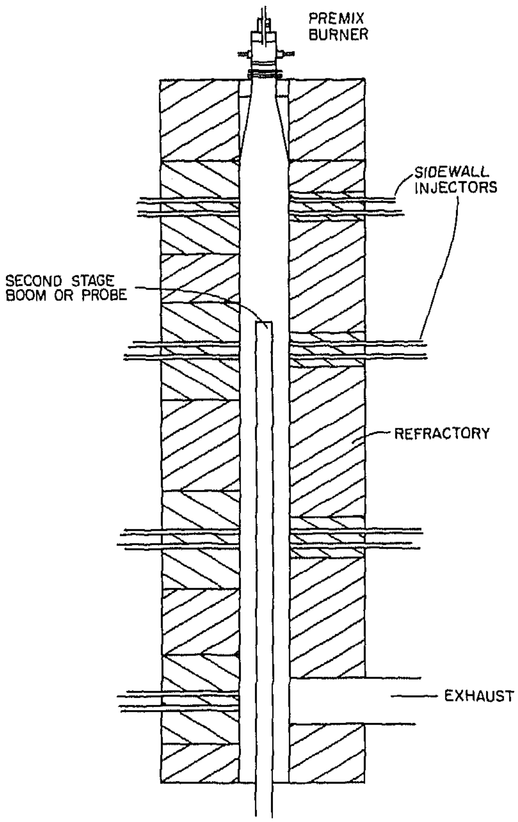

FIG. 1. Schematic of experimental combustor.

plane of injection. In-situ sampling was accomplished through an insulated, water jacketed, water quenched probe.[6]

Bulk flame temperature profiles were obtained using a specially designed suction pyrometer and by sheathed thermocouples placed in the stream and in the walls. A heat balance on the furnace, and on the pyrometer or thermocouple then allowed the corrected average temperature to be estimated.[8] This corrected temperature, reported subsequently herein, differed from that directly measured by 140°K at 1500°K and negligibly at 1100°K, and denotes a mixing temperature of gas and particles. Residence time was calculated using the corrected temperature, O_2, CO and CO_2 profiles, and a partial equilibrium for the other species, such as H_2 and H_2O, not measured.

Compositions of pulverized fuels are shown in Table 1. Ranges extend over various nitrogen and sulfur contents as well as over rank and volatile matter. The high volatile bituminous Western Kentucky coal constituted our "base fuel." The first four fuels were identical to those investigated in previous work[1][4] on NO_x from turbulent diffusion flames.

Results

Time-Resolved Profiles: Western Kentucky Coal

Time-resolved profiles of NO, O_2, CO_2, CO, unburned carbon (obtained by difference) and temperature are shown for the base coal on Figs. 2 and

TABLE 1
Pulverized fuel compositions

Ultimate analysis (% dry)	Colorado	Pittsburgh #8	Western Kentucky	Montana Powder River	Texas lignite	FMC char (low volatile)	IGT char (high volatile)
C	73.1	77.2	73.0	67.2	60.44	72.8	66.3
H	5.1	5.2	5.0	4.4	4.61	0.9	1.75
N	1.16	1.19	1.4	1.1	1.21	0.99	0.72
S	1.1	2.6	3.1	0.9	1.75	3.5	1.78
O	9.7	5.9	9.3	14.0	14.38	0.7	6.57
Ash	9.8	7.9	8.2	11.7	17.61	21.2	22.88
Heating value Btu/lb wet	12,400	13,700	12,450	8,900	6,677	—	—
Proximate analysis %							
Volatile matter	38.9	37.0	36.1	30.5	28.68	3.6	13.6
Fixed carbon	52.6	54.0	51.2	39.0	24.08	73.8	57.5
Moisture	3.3	1.2	4.8	21.2	35.96	1.8	7.8
Ash	8.9	7.8	7.8	9.2	11.28	20.8	21.1

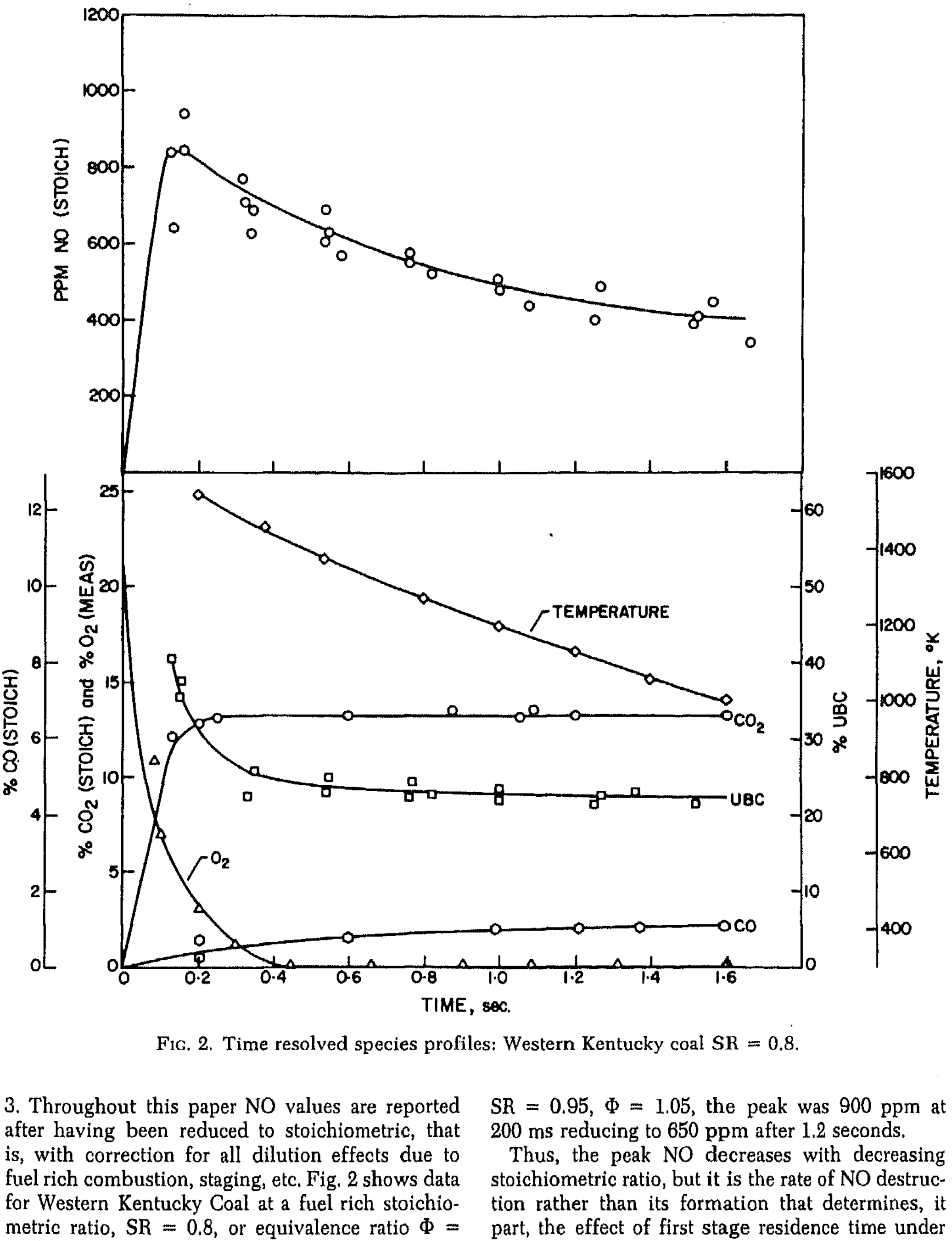

FIG. 2. Time resolved species profiles: Western Kentucky coal SR = 0.8.

3. Throughout this paper NO values are reported after having been reduced to stoichiometric, that is, with correction for all dilution effects due to fuel rich combustion, staging, etc. Fig. 2 shows data for Western Kentucky Coal at a fuel rich stoichiometric ratio, SR = 0.8, or equivalence ratio $\Phi = 1.25$. NO is rapidly formed in less than 200 ms and then reduced slowly. Some reduction occurs even in the presence of O_2. At SR = 0.4, $\Phi = 2.5$ (Fig. 3) NO is formed somewhat less rapidly but then very slowly reduced over 3 secs. Other results at SR = 1.2, $\Phi = 0.83$, (fuel lean) showed that, there, 1100 ppm (stoich) NO are formed rapidly within 200 ms but not subsequently reduced. At SR = 0.95, $\Phi = 1.05$, the peak was 900 ppm at 200 ms reducing to 650 ppm after 1.2 seconds.

Thus, the peak NO decreases with decreasing stoichiometric ratio, but it is the rate of NO destruction rather than its formation that determines, it part, the effect of first stage residence time under staged conditions.

Time Resolved Profiles: Coal Char

Time resolved measurements of NO and other species from FMC coal char combustion are shown in Fig. 4, and were made with a view to determinating the role of heterogeneous reactions in NO

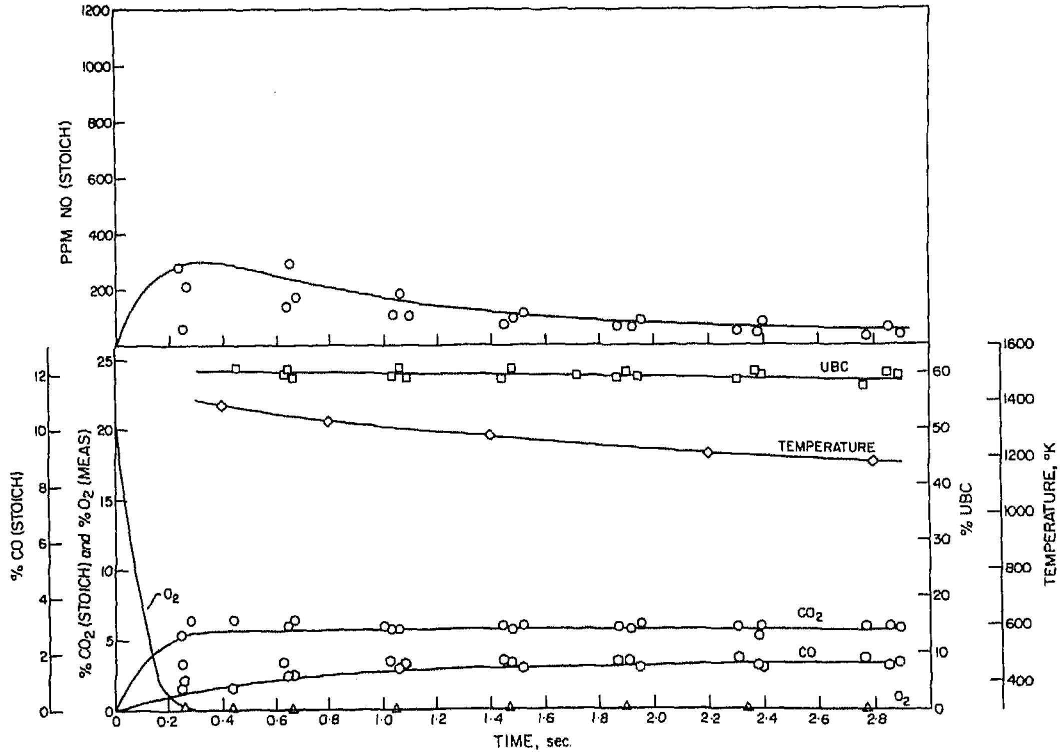

FIG. 3. Time resolved species profiles: Western Kentucky coal SR = 0.4.

formation and reduction under fuel rich conditions. Data in Fig. 4 show that this char was slow to ignite and formed a flame some distance down the combustor (at about 0.5 secs). At both SR = 0.8 and SR = 0.4, (Φ = 1.25, 2.5) NO is formed and then reduced, even though volatile matter is very small (Table 1). At SR = 0.8 a reproducible rise in NO was measured even after all O_2 had been consumed. A similar phenomenon was observed for some of the coals, but only at the less fuel rich stoichiometries.

The absence of volatiles allows the assumption that heterogeneous formation and reduction of NO are important in this experiment. Analogous profiles obtained with the IGT (high volatile) char were more similar to the coal profiles than those of the FMC char, and showed high peaks (450 ppm at SR = 0.8; 230 ppm at SR = 0.4) followed by very rapid decline, (to 190 ppm in 0.7 secs and to 50 ppm in 1.2 secs respectively). This implies that heavy volatiles, presumably characteristic of those initially in the IGT char, play an important role in NO reduction.

Staging: Time Resolved Profiles

Second stage air was injected through the opposing sidewall injectors and NO profiles were measured both upstream and downstream of the staging point. Time resolved measurement of O_2, CO, CO_2 and temperature were also made, and are reported elsewhere.(7)(8) In Fig. 5 (Western Kentucky Coal) the staging position is denoted by the vertical dashed line. The dashed profile is that of the unstaged fuel rich profile shown in Fig. 2. Stoichiometric ratios quoted are those of the first fuel rich stage. The second stage was maintained at SR_T = 1.2 (Φ = 0.83). Although there is some scatter in the data at short residence times the following phenomena exist: 1) at each staging point NO is suddenly reduced (after correction for dilution), 2) this may be followed by a slow increase in NO in the second stage.

At SR = 0.4, Φ = 2.5, (Fig. 6), the converse was true. As expected, Fuel NO increased at the staging point, although the quantity of second stage Fuel NO was only slightly sensitive to first stage residence time. This indicates the importance of the reduction of NO (and of volatile NO precursors) in the first stage. Fig. 6 shows data resulting from substitution of air by a mixture containing 21% O_2, 18% CO_2 and Ar, which allows flows and temperatures to be identical to those with air as the oxidant. The data show that both the first stage NO and the second stage NO measured at the far staging positions consisted essentially of Fuel NO. Some Thermal

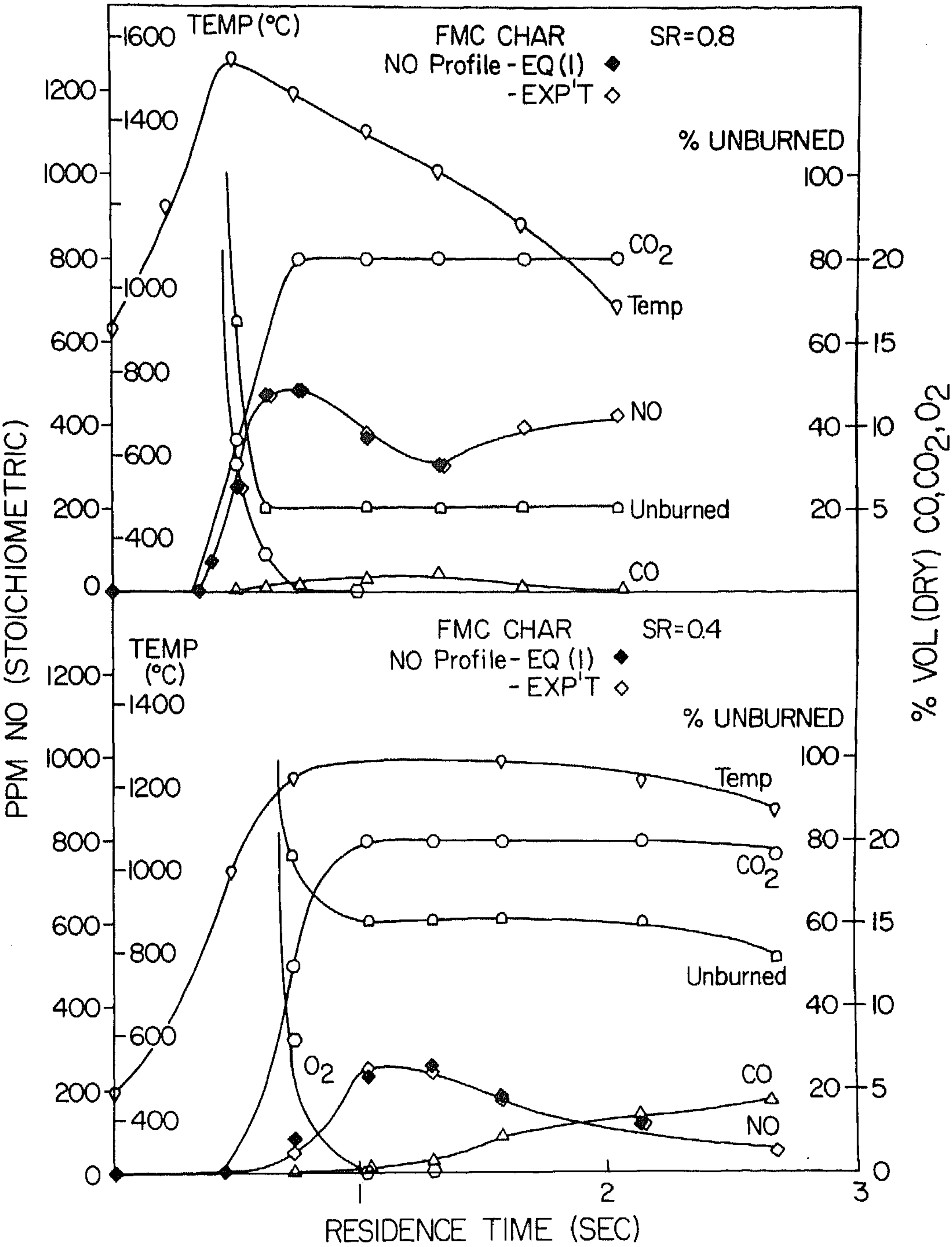

FIG. 4. Time resolved species profiles: FMC char. top: SR = 0.8; bottom: SR = 0.4.

NO may, however, be present at the first staging position.

The various influences of coal composition are shown in Figs. 7 and 8, where the vertical lines again denote the staging positions. In each case the base fuel rich profile was obtained with no staging, while the staged profiles correspond to that staging position denoted by their starting position. At SR_1

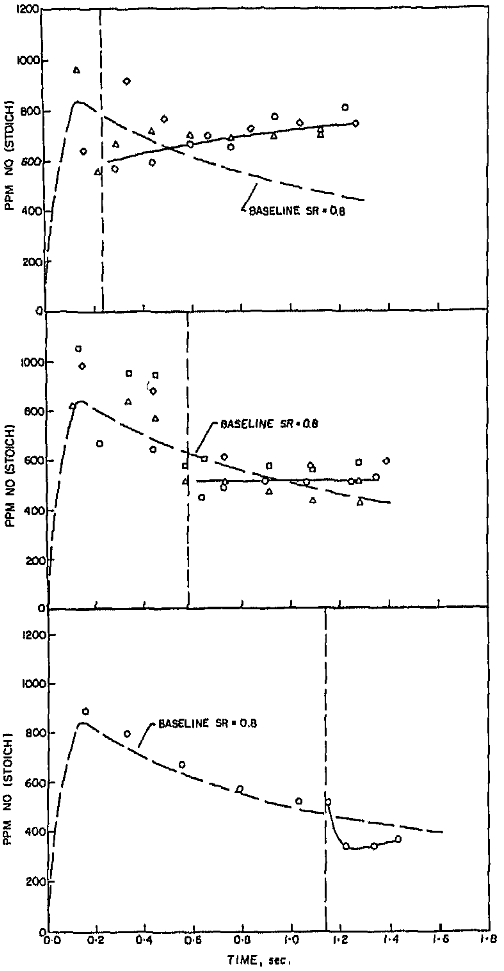

FIG. 5. Staged combustion: NO profiles. Western Kentucky coal: first stage $SR_1 = 0.8$, second stage $SR_T = 1.2$. (Staging positions denoted by vertical dashed lines).

= 0.8, $\Phi = 1.25$, the data show that:

1. The base, fuel rich, NO rates of formation and destruction are strong functions of coal composition.
2. Whether NO is destroyed or formed at the staging point is a function of both composition and first stage residence time. Large reductions (140 ppm at τ_1, 190 ppm at τ_2) in NO at the staging point were observed for the Colorado coal where the peak was high (1000 ppm) while a large increase (240 ppm at τ_1) is found in the Pittsburgh data where the peak was low (365 ppm). The Montana coal had negligible (positive or negative) Second Stage NO. Except for the Montana Coal, the NO value at the first staging position is independent of the very different base profiles and has an approximate value of 600 ppm.

The profiles at SR = 0.4, $\Phi = 2.5$, are even more dramatic in showing the influence of coal composition. The FMC char showed negligible Second Stage NO, while the Montana coal showed the greatest rapid formation of Second Stage NO (560 ppm at τ_1, 460 ppm at τ_2). In fact, comparison of Figs. 7 and 8 for the Montana coal shows the exhaust NO emissions after staging are greater at $SR_1 = 0.4$ than at $SR_1 = 0.8$ because of Second Stage NO formation. The Pittsburgh base NO profile at SR = 0.4 had very low values together with and probably because of a very rapid consumption of O_2.

Discussion

Heterogeneous Mechanisms

The FMC Char NO profiles (Fig 4) at both SR = 0.8 and SR = 0.4 can be correlated well with a simple heterogeneous reaction scheme:

$$R_{NO} = 3.3 \times 10^7 \exp\left(-\frac{54500}{RT}\right) P_{O_2}^{0.4} C_N - 4.7 \times 10^4 \exp\left(-\frac{47000}{RT}\right) X_{NO}^{0.6} W_{ASH} \cdot \left(\frac{\text{moles}}{\text{cc sec}}\right) \quad (1)$$

where

P_{O_2} = local partial pressure of oxyten (atm)
C_N = moles N in char/(volume of reactor) (assumed to be proportional to char N surface/unit volume) (moles/cm^3)
X_{NO} = *mole fraction NO*
W_{ASH} = gm ash/(cm^3 reactor) (assumed to provide the time invariant area for NO reduction and assumed to be proportional to surface area/unit volume) (g/cm^3)
T = bulk temperature, averaged over gas and particles (K).

The formation reaction activation energy is higher than that obtained by Hamor[9)] for coal char combustion, since the data show that NO is formed more slowly than O_2 is consumed. The reduction of NO is less than first order in NO, also with an appreciable activation energy.

Devolatilization

The large influence of coal composition on base NO profiles is likely to be due to different devolatilization characteristics of different coals. It is reason-

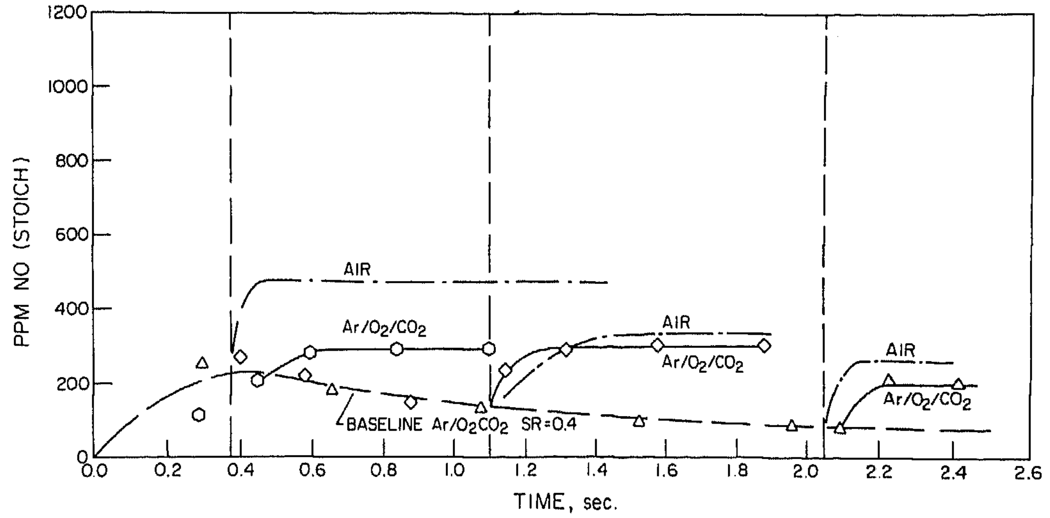

FIG. 6. Staged combustion: NO profiles. Western Kentucky coal: first stage $SR_1 = 0.4$, second stage $SR_T = 1.2$. Data show results of $AR/O_2/CO_2$ substitution.

able to speculate that, for coal, the peak NO value is determined by the quantity of early nitrogen-free volatiles available to consume oxygen prior to significant nitrogen specie evolution. It is to be expected that devolatilization rates depend on coal rank and composition.[2][3] The Pittsburgh coal data indicate rapid devolatilization of a large quantity of nitrogen-free volatiles and corresponding low NO peaks.

Correlation of coal data is therefore not likely to be a simple matter. Attempts to find one consistent set of four kinetic parameters for all the Western Kentucky data were unsuccessful because a) devolatilization of nitrogen may be a function of not only temperature, b) nitrogeneous species evolved may not be similar for all stoichiometric ratios even for one coal, c) homogeneous formation and reduction mechanisms are likely to involve hydrocarbons, and not just nitrogeneous species, d) particle size effects may be important and e) some sophistication is required to model when surface reactions begin to become important. Clearly, more data on intermediate species are required.

Homogeneous Mechanisms

In addition to heterogeneous reduction of NO, our data show that homogeneous reduction mechanisms also play a role. The reduction of NO at the staging point in the presence of O_2 points to reaction of NO and some coal-derived nitrogeneous species.[10] However, a supplementary experiment in which a small quantity of CH_4 was injected in a fuel rich coal stream after the O_2 had been consumed, showed that hydrocarbon fragments effectively lowered NO from 425 to 200 ppm. Therefore, NO reduction through the Myerson[11] reaction is also likely, since hydrocarbons can be supplied by the larger coal particles devolatizing after O_2 has been consumed. It would appear that all three heterogeneous and homogeneous reduction mechanisms can play a role in determining the fate of coal nitrogen under staged conditions.

Comparison of Second Stage NO values of the Montana, Lignite and Pittsburgh data, in Fig. 8, indicate the coal composition influences the rate at which NO precursors (volatile nitrogeneous species) are destroyed in the first stage. The Montana coal forms the greatest quantity, followed by Lignite and Pittsburgh, a trend which cannot be correlated with temperature in either the first or second stages. In each case the NO precursors, once formed, are stable and are not significantly destroyed by increasing the first stage residence time. These data suggest that different coals evolve nitrogeneous species that are distinguishable insofar as NO precursors are concerned.

Under fuel lean conditions (SR = 1.2) the NO measured (1100 ppm, stoich) correspond to a 51% conversion of volatile coal nitrogen, where the volatilized fraction of total coal nitrogen (70% at 1430°K) was obtained from weight loss data[3] on the same coal. Literature data[12] on yields of NO in premixed, fuel lean, flames indicate that minimum conversions of similar quantities of fuel nitrogen are approximately 75% or higher. Therefore, our data suggest that, even when pulverized coal is burned under overall "premixed" fuel lean conditions, volatile nitrogen is oxidized in a non-premixed environment, probably in a diffusion flame attached to each

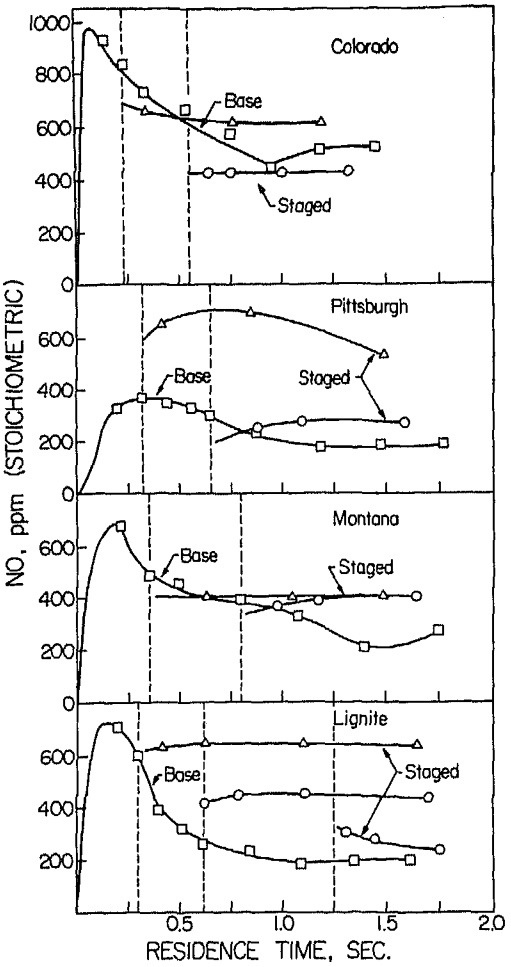

FIG. 7. Staged combustion: effect of coal composition on NO profiles at $SR_1 = 0.8$ (staging positions denoted by vertical dashed lines).

particle. This may cause difficulty in attempts to relate homogeneous fuel nitrogen kinetics to results from heterogeneous mixtures such as the ones investigated in this work.

Nomenclature

C_N	g-moles N in char/unit volume of reactor
P_{O_2}	Partial pressure of oxygen atm
R	Gas Constant = 1.987 cal/gmol °K
R_{NO}	Rate of formation of NO gmoles/cc sec
SR	Stoichiometric Ratio
SR_1	First Stage Stoichiometric Ratio
SR_T	Overall stoichiometric ratio at Second Stage
T	Absolute temperature °K
Φ	Equivalence Ratio
τ_1	First Staging position
τ_2	Second staging position
W_{ASH}	gm ash/unit volume of reactor gm/cm^3

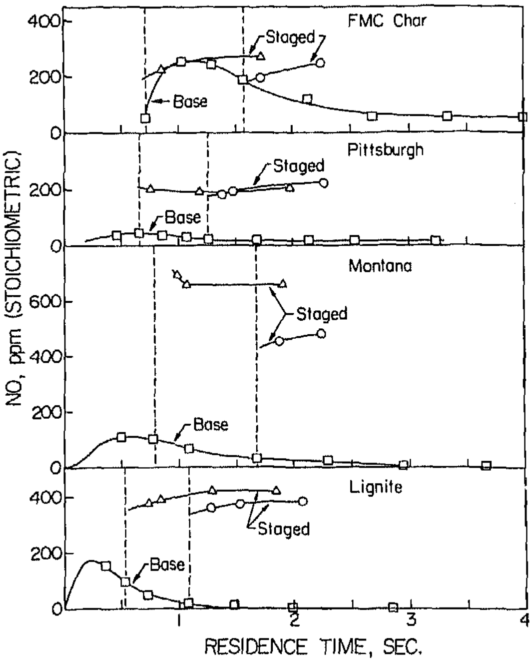

FIG. 8. Staged combustion: effect of coal composition on NO profiles at $SR_1 = 0.4$. (Staging positions denoted by vertical dashed lines).

Acknowledgments

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COMMENTS

S. A. Johnson, Babcock & Wilcox Company, USA. The disappearance of NO noted by the authors in both the first and second stage of a two-stage combustion system is remarkably similar to those that we have noted during our testing of a 4-million Btu/hr two-stage system.

Our axial concentration profiles also show that NO forms rapidly in the vicinity of the burner where the gas-phase equivalence ratio is fuel lean. Our NO peak at a first-stage stoichiometric ratio of 0.7 is only 300–350 ppm (corrected to stoichiometric conditions), presumably because we maintain a gradual mixing of fuel and air.

Once the oxygen concentration has been nearly depleted, NO begins to disappear. We have fitted this first-stage NO reduction to a pseudo first order, Arrhenius-type equation. The temperature dependency of this NO reduction is slight, but NO reduction seems to be favored by higher temperatures. The narrow range of temperatures investigated prevents an accurate measurement of this temperature dependency.

We have also measured a second-stage NO reduction under certain conditions in our combustion system. The final NO emission is only slightly dependent upon first-stage exit NO. Rather, we have found the final NO emission to be a strong function of the second-stage flame temperature and the local O_2 concentration in the flame front (degree of second-stage mixing). The second-stage NO formation or reduction takes place very rapidly and seems to be limited by chemical equilibrium. With second-stage temperatures as low as 1800°F, we could achieve NO emissions on the order of 100 ppm without significant reduction of combustion efficiency.

Have the authors postulated a reaction mechanism for either the first-stage or second-stage NO disappearance? Also, have they measured other nitrogenous species such as CN and NH compounds which can either form or reduce NO? We would like to attribute the second-stage NO reduction to an NH_2/NO reaction, but we measure very small amounts of NH_3 in our first-stage exit gas. We also wonder whether the authors have noted a similar second-stage NO temperature dependency.

REFERENCE

Johnson, S. A. and P. L. Cioffi, "Development of an Advanced Combustion System to Minimize NO_X Emissions from Coal-Fired Boilers," presented at the 1978 Joint Power Generation Conference, Dallas, Texas, September, 1978.

Authors' Reply. Your data on a four million Btu/hr, turbulent diffusion, two stage system seem, on the whole, to reinforce our conclusions obtained from a 70,000 Btu/hr, "premixed" one dimensional, plane flame combustor. There seem, however, to be some differences that are worth pointing out. Fig. 7 shows that our peak NO values were not only a function of stoichiometric ratio but also of coal composition. Therefore, at SR = 0.8 these values range from almost 1000 ppm to 400 ppm.

Our data show that, in general, the final NO after staging is not independent of the first stage exit NO. The Lignite data on Fig. 7 show this most clearly. Furthermore, we do not believe that the reduction in NO sometimes observed at the staging point is due primarily to mixing effects although these cannot be ruled out. First, our simultaneous NO and O_2 measurements indicate that second stage NO reduction occurs in the presence of O_2 and our O_2 measurements do not indicate poor mixing effects. Second, whether a reduction was observed or not depends on the coal composition, see Fig. 7, and also in some instances on first stage residence time. Presumably, second stage mixing was similar in all cases where $SR_1 = 0.8$. Our exhaust NO values, after staging, do not correlate only with temperature at the staging point (See Fig. 8), but are again strong functions of coal composition. They do not seem to be limited by chemical equilibrium. However, second stage formation or reduction of NO does occur very rapidly.

In the paper we discuss why we believe both homogeneous and heterogeneous reaction mechanisms play a role in the reduction of NO. The empirical heterogeneous expression (Eq. 1) cannot, by itself, describe the coal data but is valid only for the char.

We have not yet measured HCN and NH_3 and other nitrogenous species, but plan to do so. Clearly such information would aid in the interpretation of our data, and may help reconcile discrepancies between our data and yours.

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A. F. Sarofim, M.I.T., USA. The results of this study are extremely interesting. I wish to question the interpretation of the data on NO reduction. You chose to interpret your results assuming an ash catalyzed reaction. If this were so then why does not the NO reduction persist in the oxygen rich region beyond the point of staging? Based on previous studies in the literature one would expect both NO-char reactions, or more important, catalyzed NO/CO reactions as being major paths for NO reduction? Could you comment on the extent to which you examined these alternative NO reduction mechanisms? One could speculate that your observed reduction in NO during staging was due to a transient formation of CO which in turn augmented the NO/CO reactions.

Authors' Reply. Our empirical correlation shown on Eq. 1 is applicable only to NO formation and reduction during FMC Char combustion. It does not correlate our coal data either for the base case or for the staged profiles. In the correlation we assumed that the weight of ash/unit reactor volume was proportional to the appropriate active surface area important in NO reduction. We did not, therefore, directly exclude the char surface, but we did assume that the applicable surface area did not change with time.

If it is assumed that the rate of NO reduction is dependent on the measured CO concentration one can fit the char data on Fig. 4 by the expression

$$R_{NO} = 1.486 \times 10^7 \exp\left(-\frac{53{,}300}{RT}\right) P_{O_2}^{0.4} C_N - 1.89 \times 10^7 \exp\left(-\frac{46870}{RT}\right) X_{NO}^{0.7} P_{CO}^{0.6} W_{ASH} \qquad (1A)$$

This equation gives as good a fit to the char data as does Eq. 1. This indicates a potential pitfall in the use of empirical correlations such as these, since there will be other expressions that fit the data equally well. However, it is interesting to note that both Eqs. 1 and 1A have essentially similar activation energies and reaction orders with respect to O_2 and NO.

We agree that detailed kinetics of NO reduction during coal combustion, involve NO char reactions, catalyzed NO/CO reactions as well as homogeneous hydrocarbon NO reactions and NH_x/NO reactions. Before the detailed chemistry can be quantitatively determined, further measurements of intermediate species and evolution rates are required.

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L. D. Smoot, Brigham Young University, USA. Your results showed a large difference in NO formations among coals with staging of air vs. the base case without staging which you suggested may relate to relative rates of nitrogen and hydrocarbon evolution from the coals. Did you collect and analyze the residual coal char materials from your water-quench probe as a function of residence time?

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W. Bartok, Exxon Research and Engineering Co., USA. In the highly fuel rich combustion experiments (SR = 0.4), did you measure the concentration of other nitrogeneous intermediates? It is my feeling that the correlation of these species concentrations with the changes in NO concentration is most important for understanding the NO concentration changes.

Authors' Reply. Our data showed a large influence of coal composition on the NO profiles both under base case and staged combustion conditions. We attributed this to differences in nitrogen and hydrocarbon evolution rates for the various coals examined. We have not yet made the analysis you mention, and we strongly concur that such analyses are crucial for the unambiguous interpretation of our data.

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J. J. MacFarlane, Imperial College, England. In using $Ar/O_2/CO_2$ mixtures as a substitute for N_2, you do not state the composition. This technique is a quite well known one for raising maximum flame temperature.

Authors' Reply. The $Ar/O_2/CO$ mixture used consisted of 21% O_2, 18% CO_2 and the balance Ar. This mixture allows flows, and adiabatic flame temperatures to be matched to those for the air case, as described in earlier work [Ref. 1].