FE-1817-5
Distribution Category UC-90e

POLLUTANT CONTROL THROUGH STAGED COMBUSTION OF PULVERIZED COAL

Technical Progress Report
For Period January 1978 - April 1978

J.O.L. Wendt, J.W. Lee and J.W. Glass

Department of Chemical Engineering
College of Mines
University of Arizona
Tucson, Arizona 85721

June 1978

Prepared for the United States Department of Energy
Under Contract E49-18-1817

ABSTRACT

A 2Kg/h pulverized fuel plane 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 the NO formed in the first and second stages consisted of Fuel NO.

Heterogeneous formation and reduction of NO during char combustion was modeled by a two-reaction scheme. 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.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the help of David W. Pershing, Philip DePastena and James W. Frohlich for their participation in this project. Assistance rendered by the college mechanist Mr. Dick van Reese, and by the secretary Mrs. Sandralyn M. Faust is also gratefully acknowledged.

1.0 OBJECTIVES AND SCOPE

The objectives of this research contract are to:

1) Establish quantitatively the dependence of total and fuel NO_x emissions on combustion zone temperature, coal composition and local oxygen level in swirling, turbulent pulverized coal flames.

2) Define the optimum application of classical staged combustion as a means of lowering pollutant emissions from pulverized coal firing.

3) Estimate the relative importance of thermal NO, volatile NO and char NO under a variety of normal and staged combustion conditions.

4) Analyze resulting data in order to obtain general insight into fuel nitrogen conversion during pulverized coal combustion with a view of developing scale up criteria to be used for NO_x abatement from practical combustion units.

In order to meet these objectives the program work scope was divided into three identifiable tasks shown in Table 1. Task 1, NO_x Formation in Swirling Turbulent Pulverized Coal Flames has been completed and results reported elsewhere in reports FE1817-1 and FE1817-2. Task 3, except for correlation development, is also complete and results have been reported in FE1817-3. Portions of Task 2 are reported in FE1817-4. This report is concerned with the remainder of Task 2, and focusses on Mechanism Characterization and Effect of Coal Composition. Some correlation is also included. Therefore, this report is concerned with Contract Tasks Numbers 4,5 and 6 as shown on Table 1.

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.

TABLE 1.1 TASK COMPLETION CHART FOR CONTRACT E(49-18)-1817

Technical Program Organization		Contract Task Numbers	Percent Completed 4/30/78	Results Reported
TASK 1.0	NO_x Formation-Swirling, Turbulent Pulverized Fuel Flames			
1.1	Combustor Characterization	Tasks 1 & 2	100%	FE1817-1 & 2
1.2	Fuel NO_x Definition	Task 9	100%	FE1817-1 & 2
1.3	Coal Composition Studies	Task 10	100%	FE1817-2
1.4	Temperature Investigation	Task 11	100%	FE1817-2
TASK 2.0	NO_x Formation-Staged Combustion Systems			
2.1	Staging Evaluation	Task 3	100%	FE1817-4
2.2	Mechanism Characterization	Task 4	80%	FE1817-4 and this report
2.3	Effect of Coal Composition	Task 6	80%	This report
TASK 3.0	Analysis			
3.1	Char and Volatile Nitrogen Definition	Task 12	100%	FE1817-3
3.2	Local O_2 Dependence	Task 13	100%	FE1817-1, 2 & 3
3.3	Correlation Development	Task 5	80%	FE1817-3 and this report

The focus of this research is to identify experimentally the phenomenological NO_x formation mechanism 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 research1) 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 experiments2)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 experiments4) 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, 2Kg/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 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 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. 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". Fuels #1, 2, 3 and 4 were identical to those investigated in previous work[1)4)].

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

TABLE 1: Pulverized Fuel Compositions

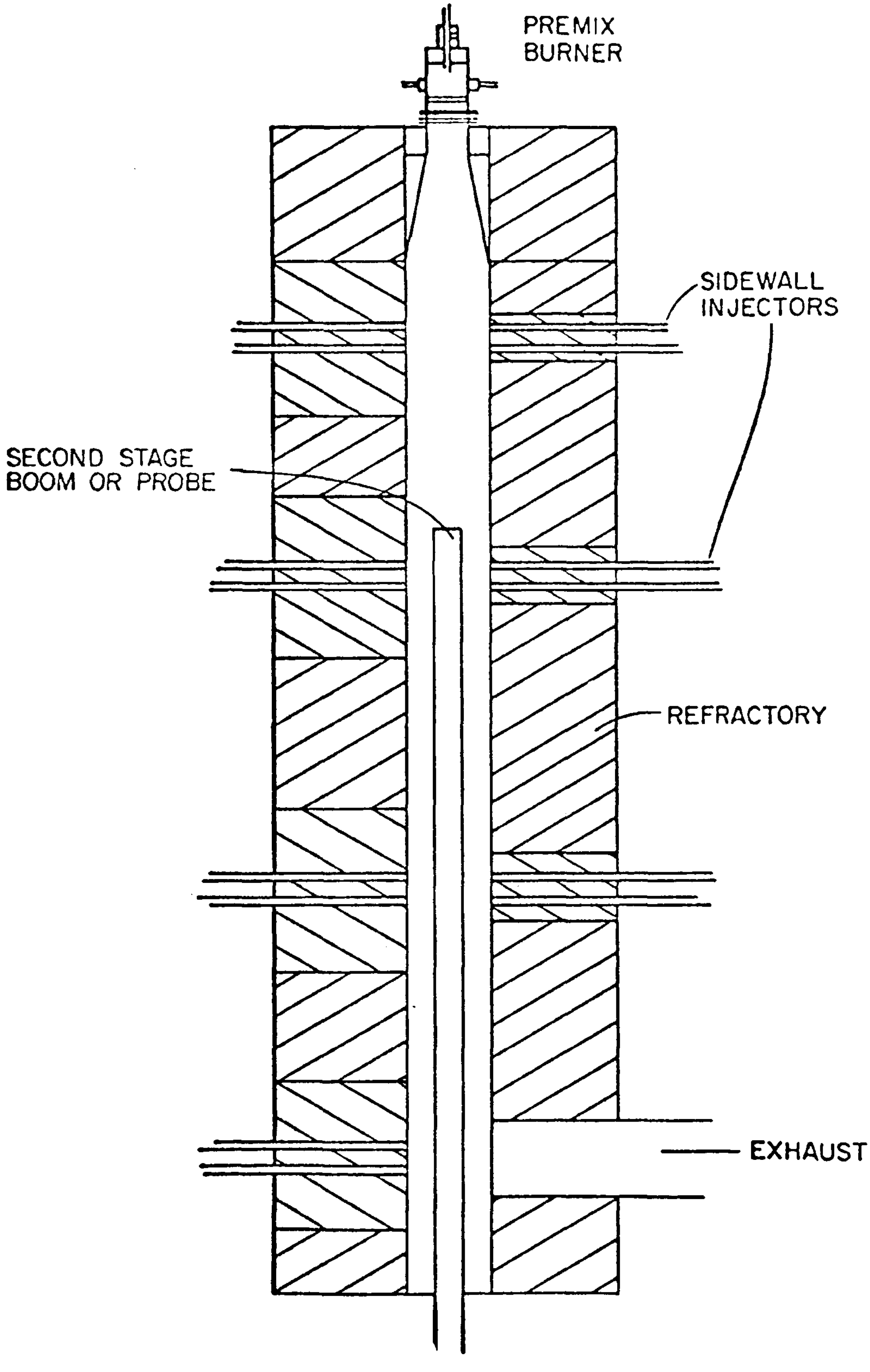

Fig. 1. Schematic of Experimental Combustor

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 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. 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 (Fig. 3) NO is again formed somewhat less slowly but then very slowly reduced over 3 secs. Other results at SR = 1.2 (fuel lean) showed that, there, 1100 ppm (stoich) NO are formed rapidly within 200 ms but not subsequently reduced. At SR = 0.95 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, in 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 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, NO is formed and then reduced, even though volatile matter is very small (Table 1). At SR = 0.8 a reproducible

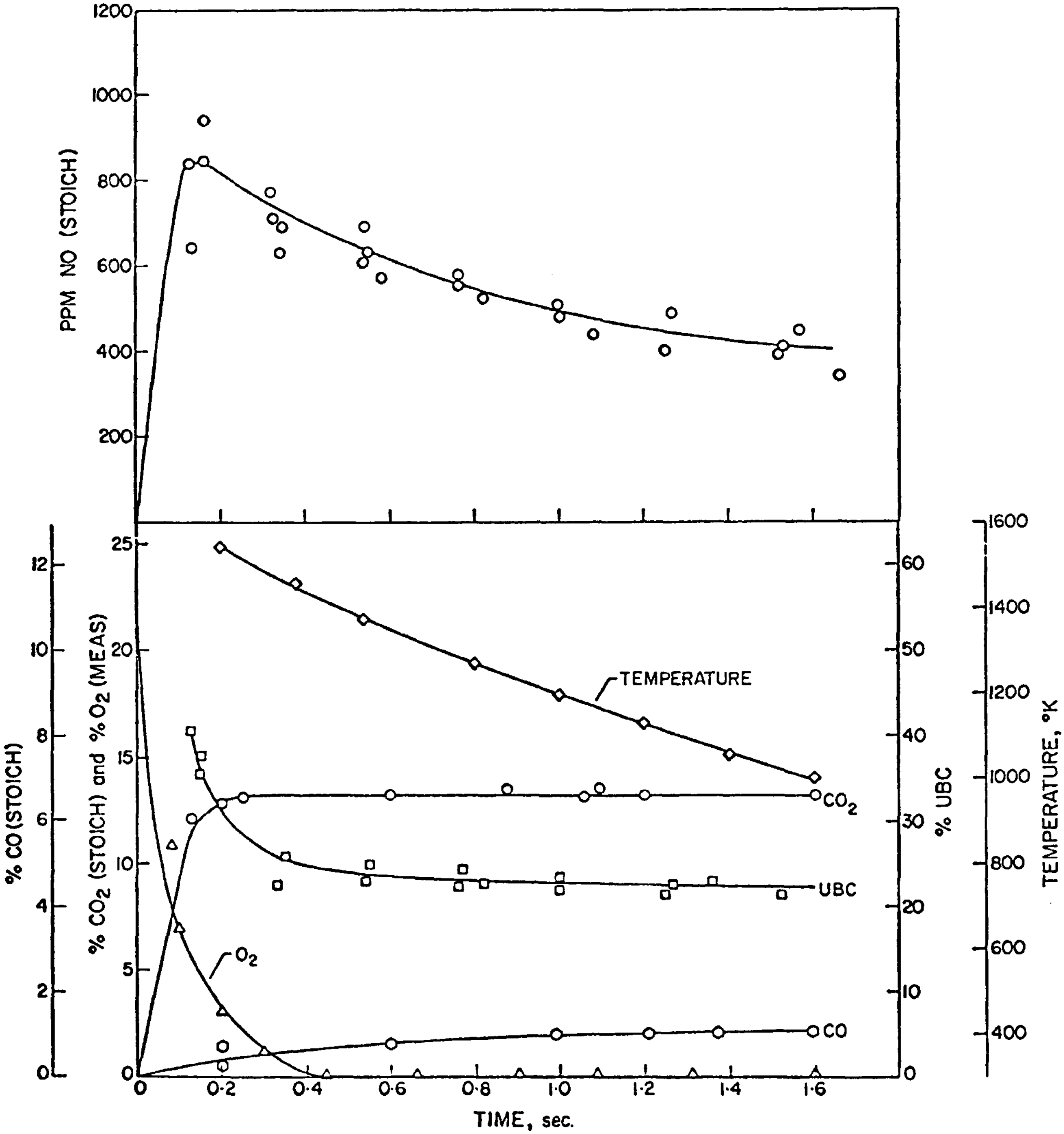

Fig. 2. Time Resolved Species Profiles: Western Kentucky Coal SR = 0.8

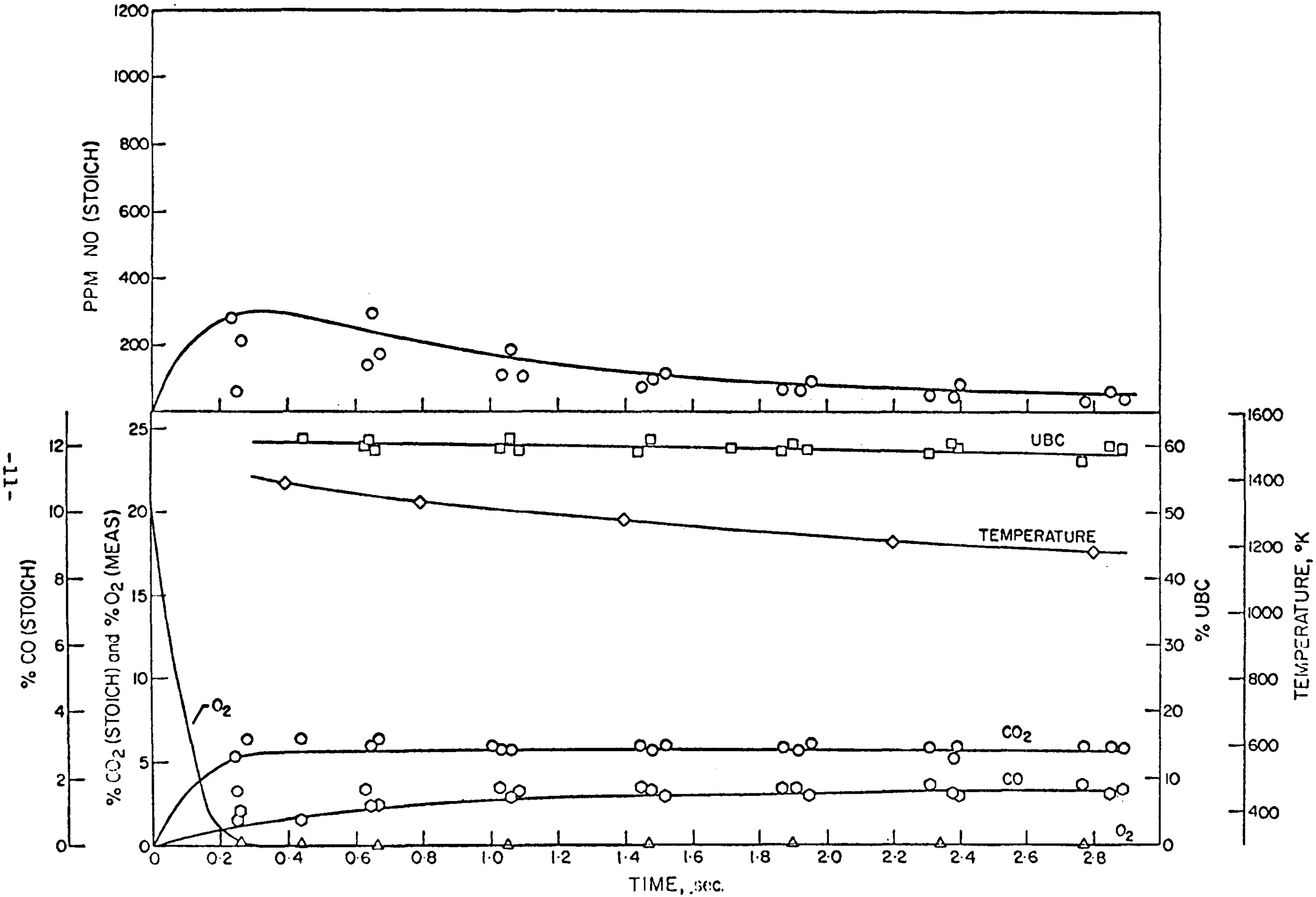

Fig. 3. Time Resolved Species Profiles: Western Kentucky Coal SR = 0.4.

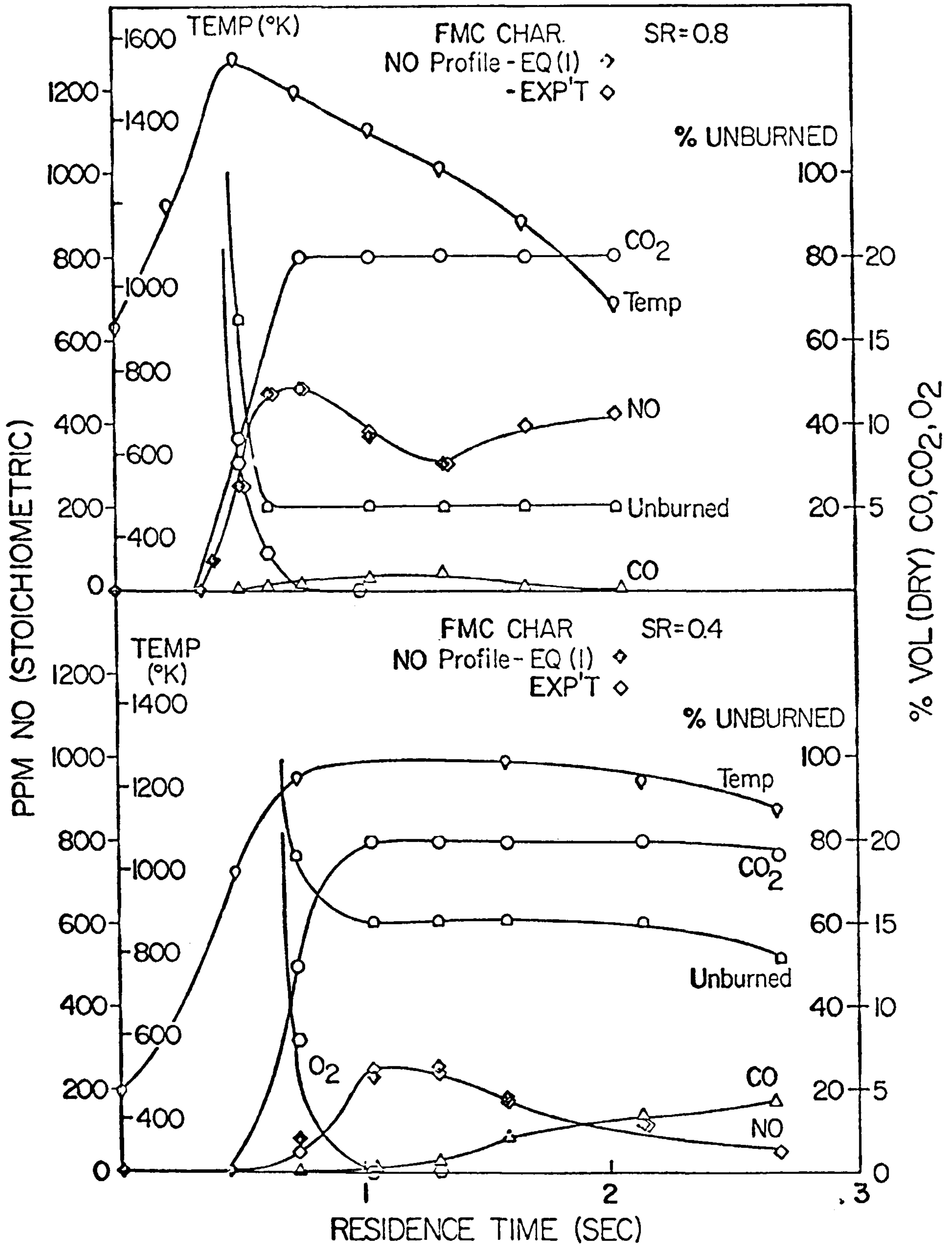

Fig. 4. Time Resolved Species Profiles: FMC Char
Top: SR = 0.8; Bottom: SR = 0.4

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. 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 $SR_T = 1.2$. 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. Other experiments6) in which air was substituted by an $Ar/O_2/CO_2$ mixture indicated that these were Fuel NO profiles.

At SR = 0.4 (Fig. 6), the converse was true. As expected, Fuel NO increased at the staging point, although the quantity of second stage Fuel NO was insensitive 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

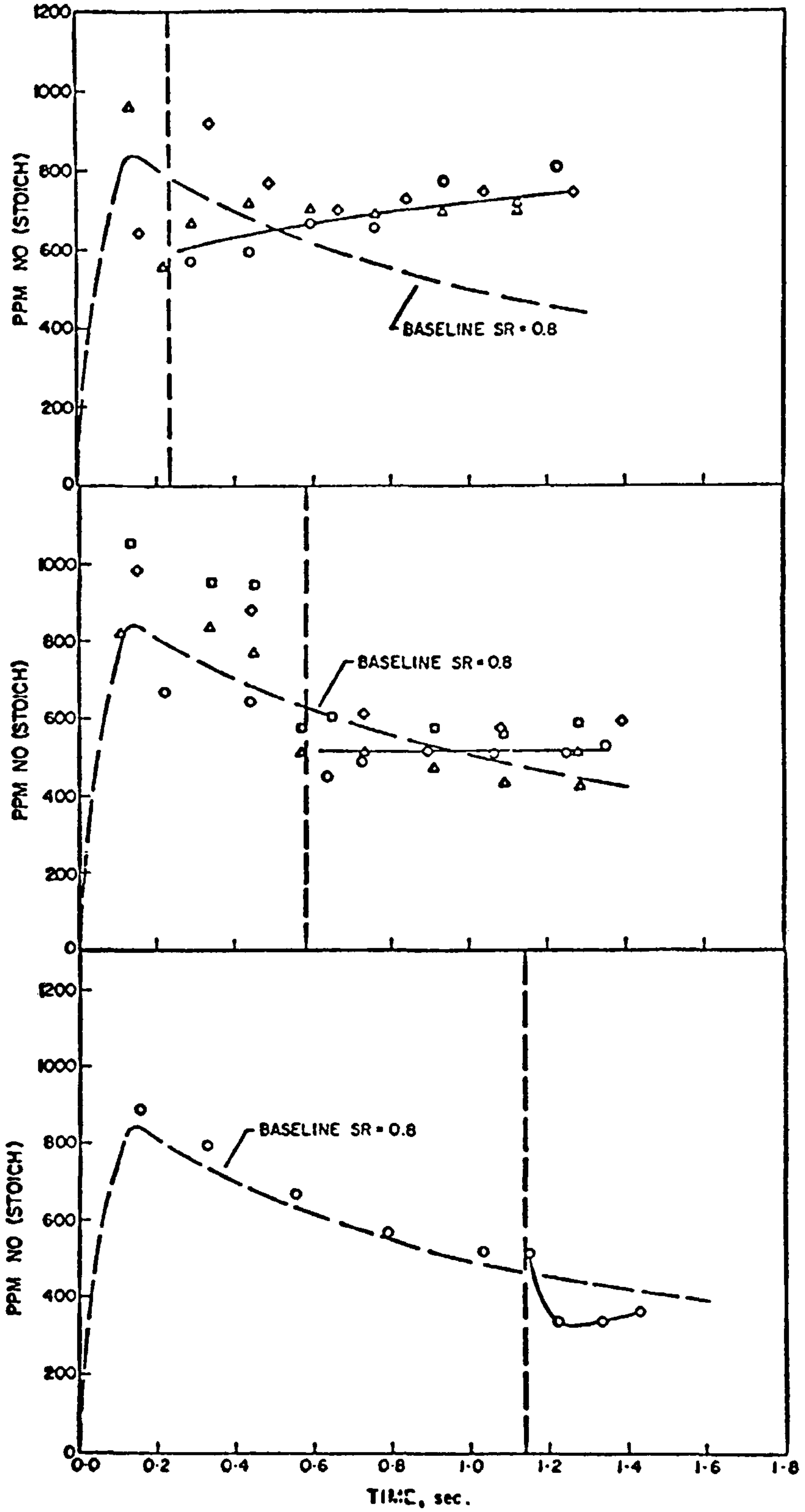

Fig. 5. Staged Combustion: NO Profiles. Western Kentucky Coal: First Stage $SR_1 = 0.8$, Second Stage $SR_T = 1.2$. (Staging Positions denoted by vertical dashed lines)

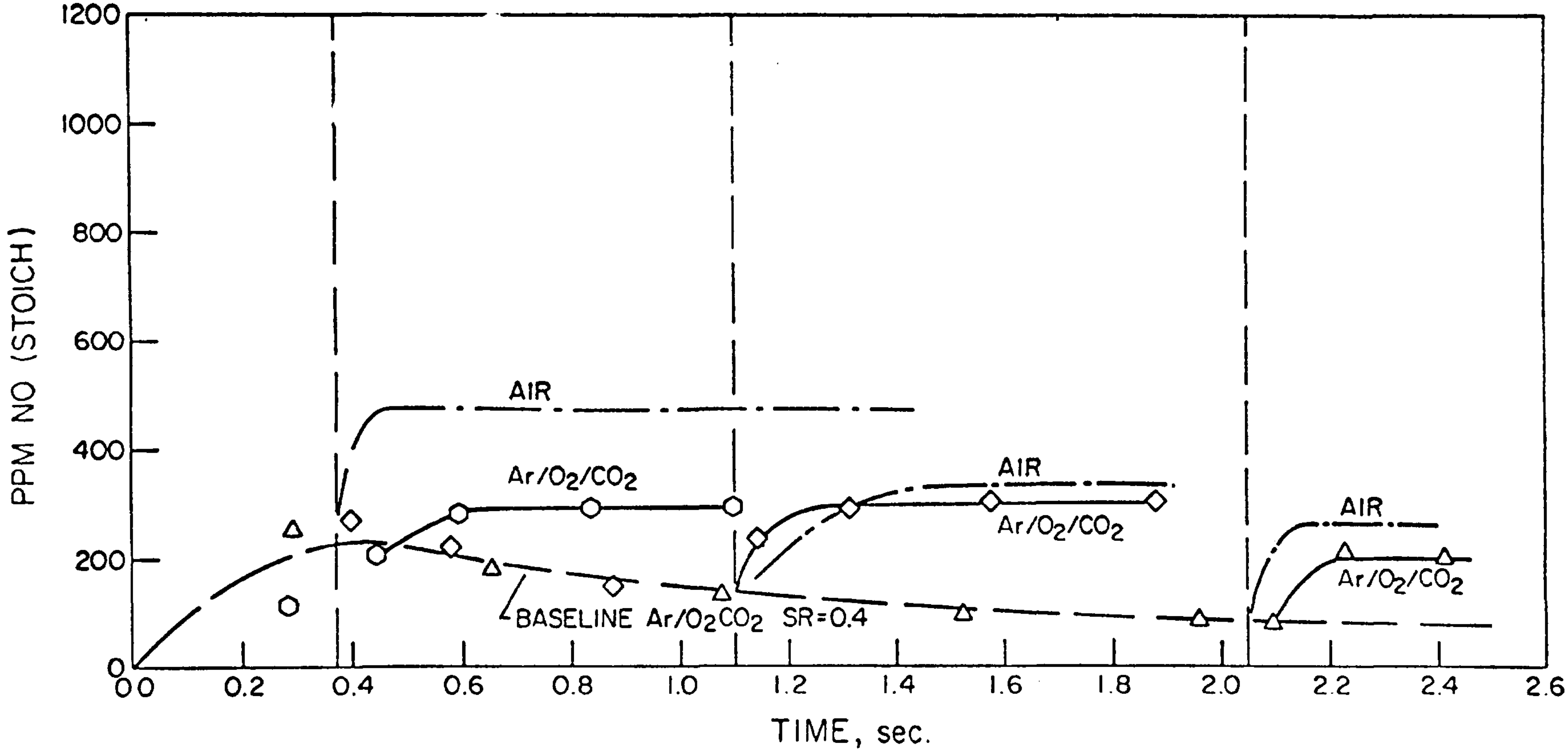

Fig. 6. Staged Combustion: NO Profiles. Western Kentucky Coal: First Stage $SR_1 = 0.4$, Second Stage $SR_T = 1.2$. Data show results of $Ar/O_2/CO_2$ substitution.

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 and second stage NO measured consisted essentially of Fuel NO.

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 $SR_1 = 0.8$ 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 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 that 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.

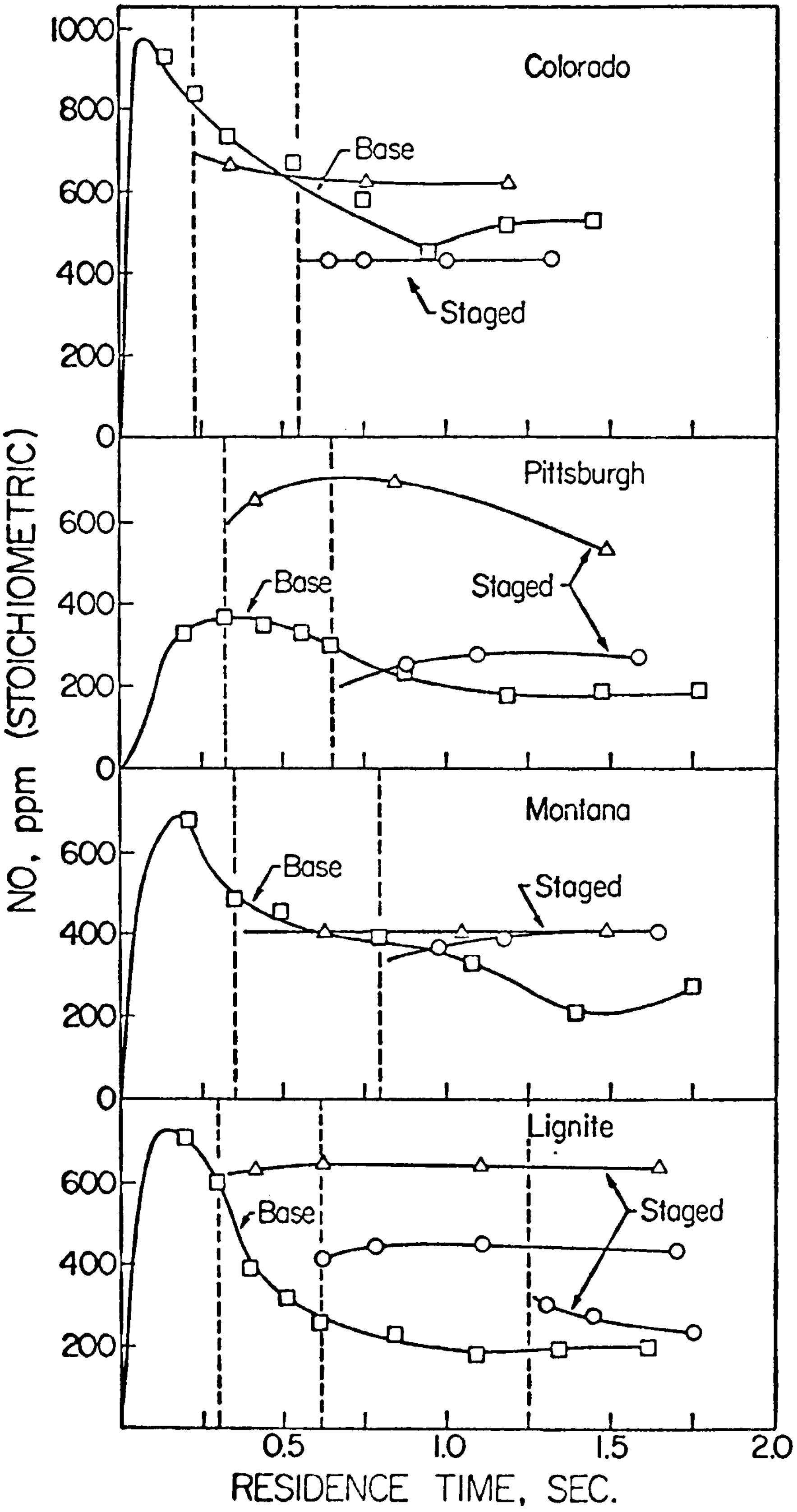

Fig. 7. Staged Combustion: Effect of Coal Composition on NO Profiles at $SR_1 = 0.8$ (Staging positions denoted by vertical dashed lines)

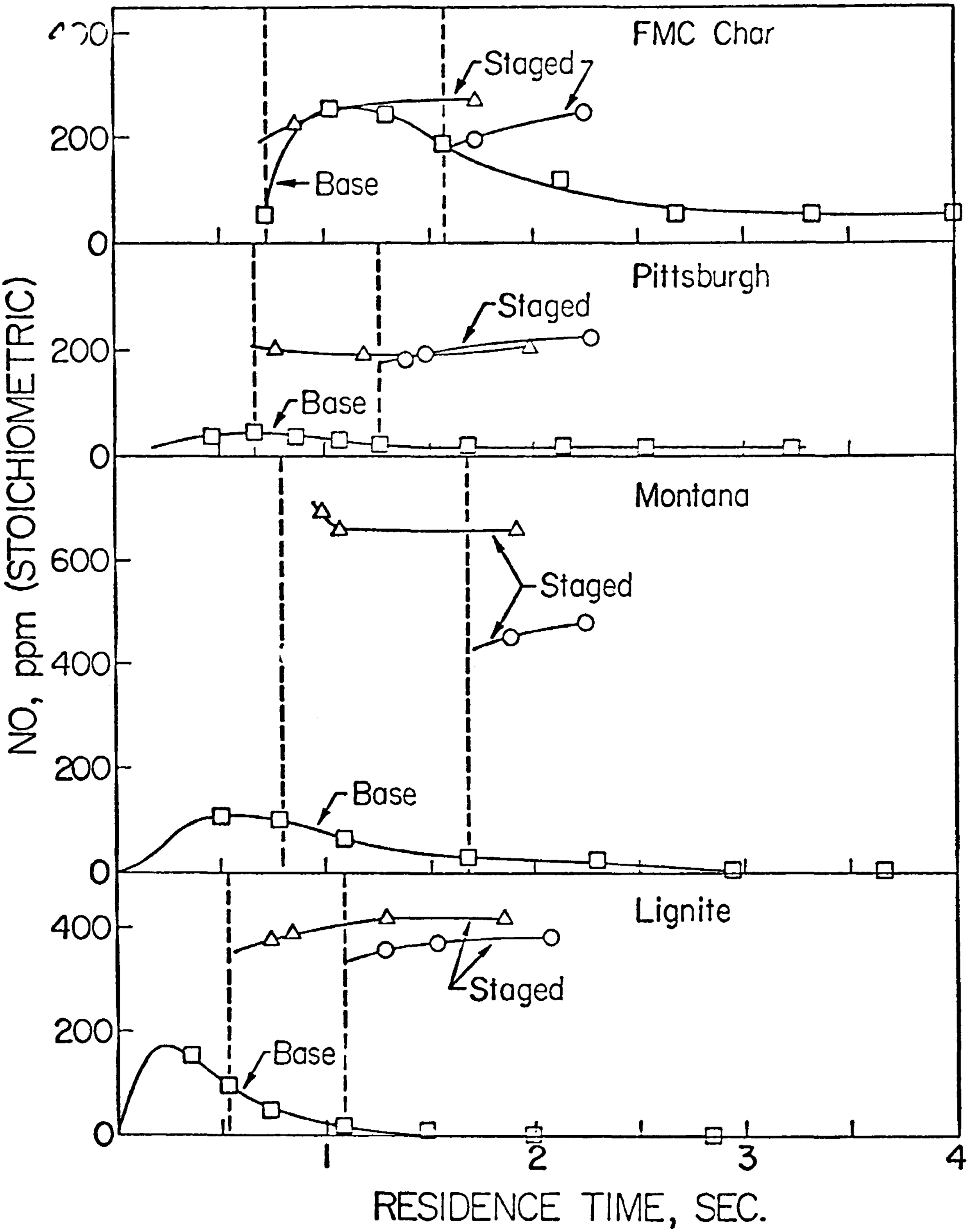

Fig. 8. Staged Combustion: Effect of Coal Composition on NO Profiles at $SR_1 = 0.4$. (Staging positions denoted by vertical dashed lines)

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:

$$R_{NO} = 3.3 \times 10^{7} \exp\left(-\frac{54500}{RT}\right) P_{O_2}^{\;0.4}\, C_N$$

$$- 4.7 \times 10^{4} \exp\left(-\frac{47000}{RT}\right) X_{NO}^{\;0.6}\, W_{ASH} \quad \left(\frac{\text{moles}}{\text{cc sec}}\right) \qquad (1)$$

where

P_{O_2} = local partial pressure of oxygen (atm)

C_N = moles N in char/(volume of reactor) (assumed to be proportional to char N surface/unit volume) $\left(\frac{\text{moles}}{\text{cm}^3}\right)$

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)

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 coal. It is reasonable 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 composition2)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 species10). 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 Myerson11) 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 that 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 each case the 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 data3) on the same coal. Literature data12) 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 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 $^{cal}/_{gmol}$ ^{o}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 ^{o}K
τ_1	First Staging position
τ_2	Second staging position
W_{ASH}	$^{gm\ ash}/_{unit\ volume\ of\ reactor}$ $^{gm}/cm^3$

REFERENCES

1) 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" Sixteenth Symposium (International) on Combustion, p. 389. The Combustion Institute, Pittsburgh, Pennsylvania (1977).

2) Pohl, J.H. and A.F. Sarofim, "Devolatilization and Oxidation Of Coal Nitrogen", Sixteenth Symposium (International) on Combustion, p. 491 The Combustion Institute, Pittsburgh, Pennsylvania (1977).

3) Blair, D.W., J.O.L. Wendt and W. Bartok "Evolution of Nitrogen and other Species during Controlled Pyrolysis of Coal", Sixteenth Symposium (International) on Combustion, p 475 The Combustion Institute, Pittsburgh, Pennsylvania (1977).

4) Brown, R.A., M.B. Mason and P. Neubauer "Investigation of Staging Parameters for NO_x Control in Both Wall Fired and Tangentially Coal Fired Boilers" Proc of the Second Stationary Source Combustion Symposium, Vol III, EPA Publication EPA-600/7-77-073c, p. 141 (1977).

5) Howard, J.B., and R.H. Essenhigh. "Pyrolysis of Coal Particles in Pulverized Fuel Flames." Ind. Eng. Chem. Process Design and Development, 6 1 (1967).

6) Wendt, J.O.L., J.W. Lee and D.W. Pershing, "Pollutant Control Through Staged Combustion of Pulverized Coal" U.S. Department of Energy, Technical Progress Report FE-1817-4 February 1978, available from Technical Information Center, Oak Ridge, Tenn.

7) Kamotani, Y and I. Greber, "Experiments on a Turbulent Jet in a Cross Flow" AIAAJ 10, 11 (1972).

8) Glass, J.W. "Mechanistic Guidelines for the Control of Nitrogen Oxides by Staged Combustion of Pulverized Coal". MS Thesis, University of Arizona (1978).

9) Hamor, R.J., I.W. Smith and R.J. Tyler, Comb. Flame 21 p 153-162 (1973).

10) Lyon, R.K. and J.P. Longwell, "Selective, Non-Catalytic Reduction of NO_x by NH_3". Proceedings of the NO_x Control Technology Seminar, February 1976, EPRI Report SR-39 Palo Alto, California 94304

11) Myerson, A.L. "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures". Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1975).

12) DeSoete, G.G. "Overall Reaction Rates of NO and N_2 Formation from fuel Nitrogen", Fifteenth Symposium (International) on Combustion, p. 1093, The Combustion Institute, Pittsburgh, Pennsylvania (1975).

*U.S. GOVERNMENT PRINTING OFFICE: 1979-640-014/4489. Region 4.