PULVERIZED COAL COMBUSTION: THE INFLUENCE OF FLAME TEMPERATURE AND COAL COMPOSITION ON THERMAL AND FUEL NO$_x$

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A laboratory combustor was used to investigate the factors that influence the conversion of fuel nitrogen in coal during coal combustion. Fuel NO was isolated by experimentation utilizing Argon/Oxygen/Carbon Dioxide mixtures as the oxidant, and care was taken to compare cases with air at matched conditions. For both well mixed and slowly mixed flame types, fuel NO contributed over 75% of the total NO emissions for all conditions examined. Fuel NO was insensitive to temperature changes except when the adiabatic flame temperatures were above 2480°K (4000°F). At the highest adiabatic flame temperature, 2580°K (4200°F), a 10% increase in fuel NO was observed.

Four different coals and one coal char were investigated. Fuel NO could not be correlated with fuel nitrogen content alone, even though aerodynamic conditions were kept constant. Fuel nitrogen conversion to NO during pulverized char combustion was 12-16% at a stoichiometric ratio of 1.15 compared to 28% for a pulverized coal of the same nitrogen content. Furthermore, in contrast to the coal results, NO emissions from char combustion were not greatly influenced by changes in injector design. The implication is that although conversion of fuel nitrogen to NO may be relatively low during the char burnout regime of coal combustion, the residual "char NO" may be especially resistant to abatement by modifications of the burner aerodynamics.

Introduction

One of the problems associated with pulverized coal combustion is the emission of nitrogen oxides, a significant fraction of which is postulated to originate through oxidation of chemically bound nitrogen in the fuel.[1] Bituminous coal, subbituminous coal and even coal char tend to have fuel nitrogen contents of about 0.8-2% by weight, yet it has not been established what fraction of this fuel nitrogen is oxidized to NO during a typical combustion process. Field test data[2] on the dependence of NO$_x$ emissions on load has led to the inference that fuel nitrogen contributes fifty percent of the emission at full load. However, changes in load on a full scale unit are usually accompanied by variations in aerodynamics which tend to obscure results as far as fuel nitrogen is concerned. In order to identify the correct phenomena, it is necessary to obtain NO emission data taken from self sustaining pulverized coal flames but under controlled conditions. Very little such data on solid fuels is available,[2] and the existence of fuel NO from coal, in particular, has been confirmed only at very high temperatures.[3] Further confusion arises because of discrepancies between the observed effect of air preheat[3] and the hypothesis that the temperature dependence of fuel NO from pulverized coal is slight; yet knowledge of this temperature dependence is critical, since argon substitution for air (used to eliminate thermal NO) leads to significantly higher flame temperatures.

This work focuses on the role of flame temperature and coal composition (including coal char) on both thermal and fuel NO from controlled self sustaining pulverized fuel flames. The intent is both to provide general insight applicable to practical combustion systems and to help identify which phenomena require further investigation through basic studies. To meet these dual objectives we consider as primary variables the roles of flame temperature, coal composition and coal char,

and include a detailed discussion of the role of burner hardware changes only insofar as these changes allow the above phenomena to be investigated for two widely different flame types of practical interest. A detailed discussion on the important role of aerodynamics and mixing on fuel nitrogen conversion from coal combustion is outside the scope of this work.

Although it has been postulated[4] that the temperature dependence of homogeneous oxidation of nitrogenous compounds is slight, these results cannot be directly extrapolated to coal combustion because both particle temperature and particle heating rate[5] influence the fraction of fuel nitrogen that is devolatilized and the fraction that remains in the char[6] during combustion. Indeed, variations of the physical behavior of coal due to differences in type and rank might also be expected to influence the fate of fuel nitrogen during coal volatilization.

The fate of fuel nitrogen in char is of interest for two reasons: first, coal char is produced during coal gasification and can be utilized by combustion to raise steam; second the char burnout regime is important during pulverized coal combustion, and for this reason the role of char nitrogen has been theoretically investigated.[7] In this work we sought to determine how much of the fuel nitrogen in char was converted to NO, since that information would indicate whether it was desirable to modify coal combustion conditions to alter the nitrogen distribution between volatiles and char.

Our approach was experimental and utilized a laboratory combustor which allowed a self-sustaining pulverized coal flame to be maintained. A methodology was developed which allowed the relative level of thermal and fuel
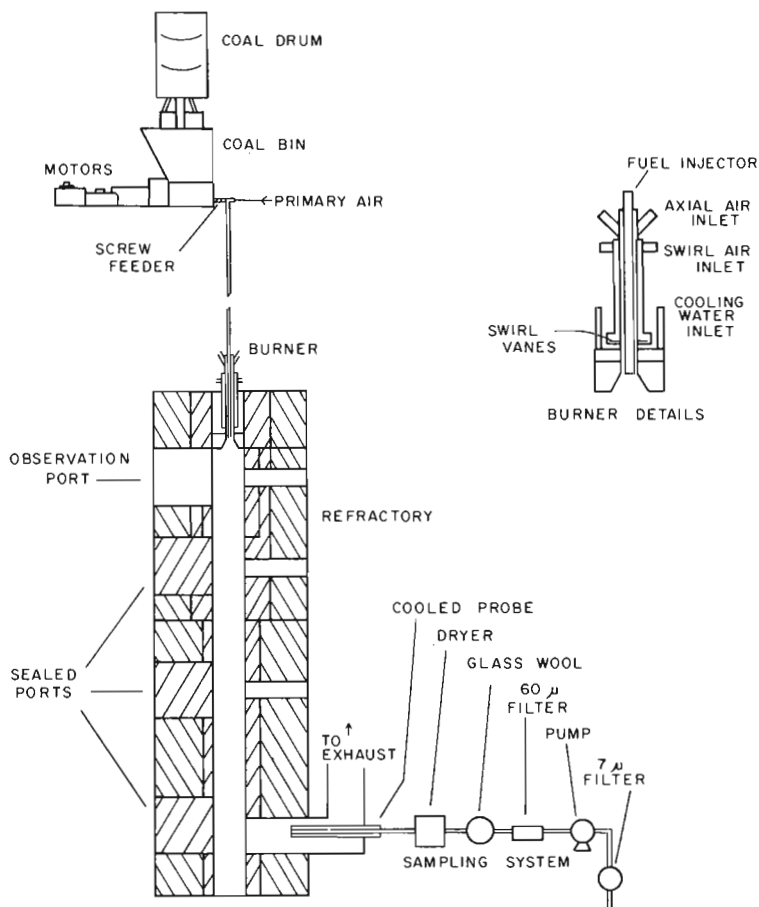

FIG. 1. Experimental combustion facility

NO to be determined under essentially identical combustion conditions, and which allowed the factors which influence fuel nitrogen conversion during coal and coal char combustion to be examined.

Combustion Facility

Furnace

The experimental furnace is illustrated in Figure 1. It was designed to contain the salient features of practical combustion hardware and yet be sufficiently well defined so that one variable could be changed at a time. The vertical combustion chamber was 1.86 m (76″) long and 15 cm (6″) in diameter inside. The overall outer diameter was approximately 69 cm (27″). Walls consisted of an outer steel shell, two layers of roll board insulation, and about 25 cm (10″) of insulating and high temperature castable refractories.

At the full load firing rate of 25 kw (85,000 Btu/hr) the cylindrical combustion chamber provided a nominal residence time of approximately one second. Four 15 cm × 25 cm observations ports and three 5 cm diameter ports spaced down the length of the furnace allowed flame photography, visual observation, and optical wall temperature measurements. These ports could be sealed by removable plugs.

Under normal operating conditions, a 690 kPa (100 psig) air compressor provided the combustion air. For special tests the "air" was enriched or replaced with varying amounts of carbon dioxide (CO_2), argon (Ar), and oxygen (O_2) all of which were supplied from high pressure cylinders. The primary "air" (used to convey the coal) was metered with a rotameter and was not preheated. The secondary "air" was metered with a laminar flow element and preheated with an electric circulation heater. When desired, filtered flue gas could be recycled and added into the secondary "air" stream just prior to the electric preheater. The furnace was under positive pressure at all times.

The pulverized coal was metered with a twin-screw feeder mounted above the furnace. Uniform coal flow was obtained by operating the feeder at maximum rpm and by impinging a high velocity air jet onto the screw outlet.

Burner

Fuel and air entered the combustion chamber through the water-cooled burner illustrated in Figure 1. It had separate axial and swirl air inlets and was similar to that used in previous studies.[3] The axial air entered through two angled ports into the center pipe. Swirl air entered a vaned swirl chamber through two tangential ports, 180 degrees opposed, and passed through curved swirl vanes. Percent swirl was defined as the ratio, in percent, of the volumetric flow of air introduced through the swirl vanes to the total secondary air volumetric flow rate. The burner throat was water cooled and the exit was fitted with a 30 degree refractory quarl with an L/D ratio of one.

The burner could accept two different fuel injector types. The first contained three holes angled to distribute the coal away from the axis of the furnace and was characterized as a rapid mixing injector because it produced short bulbous flames. It was designed to be similar to the "coal spreader" system employed in many commercial systems. The second injector contained a single center hole with an area equal to that of the three holes in the divergent injector. It produced relatively slow mixing between the primary and secondary air streams and hence gave a long, very thin flame. The two injectors were thus somewhat representative of two different classes of coal combustion equipment—one with intense mixing common in wall fired units, the other with slow mixing common in tangentially fired units.

Analytical System

The sampling and analysis system allowed for continuous monitoring of NO, NO_2, CO_2, O_2 and SO_2 using the instruments listed in Table I. The flue gas was withdrawn from the stack through a 9.5 mm (3/8″) ID water-

TABLE I
Pollutant analysis

NO	Thermo Electron Model 10AR Chemiluminescence Analyzer
NO_2	Stainless steel and Molybdenum Converter
O_2	Beckman Model F3 Paramagnetic O_2 Analyzer
O_2	Beckman Model 715 Polarographic O_2 Analyzer
CO	Beckman Model 864 NDIR CO Analyzer
CO_2	Beckman Model 864 NDIR CO_2 Analyzer
SO_2	Thermo Electron Model 40 Pulsed Fluorescence Analyzer

cooled stainless steel probe. During initial shakedown the water-cooled stainless steel probe was compared with both cooled and uncooled quartz probes. No difference in the measured NO was noted, even with CO and unburned carbon present. It should be noted, however, that the flue gas had cooled to below 800°K at the point of sampling and there was always at least 0.5% oxygen present in the sample.

Sample conditioning prior to the instrumentation consisted of a refrigerated dryer (water condenser), two glass wool filters, a 60μ stainless steel filter (283°K), a stainless/teflon sampling pump and a 7μ stainless filter. All sample lines were 6.3 mm (1/4") teflon and all fittings 316 stainless steel.

Fuels

Analyses of the four coals and the coal char used in this study are given in Table II. The Colorado coal was the same coal used in a previous study.[8] The Colorado, Pittsburgh #8, and Western Kentucky were all medium volatile bituminous coals while the Montana-Powder River Region coal was a subbituminous coal containing significant moisture. This selection of four coals allowed effects of variations in geographic origin, rank, sulfur content

and nitrogen content to be investigated. All of the coals were pulverized to approximately 75% through 200 mesh. The coal char originated from the FMC-COED coal gasification process, and was subsequently ground to 70% through 100 mesh.

Results

Fuel NO and Thermal NO

Fuel NO was isolated by using, instead of air, a synthetic oxidant mixture containing 21% O_2, 18% CO_2 and 61% Argon. This allowed theoretical flame temperatures to be matched between preheated (530°K) air and unpreheated $Ar/O_2/CO_2$ cases at a stoichiometric ratio, SR, of 1.15. Burner sleeves were available to ensure that inlet velocities and therefore flow patterns could also be approximately matched, but our preliminary tests indicated that they were not required since small variations in secondary air velocity had negligible effect. Low CO emission levels (<400 ppm) and good agreement between O_2, CO_2 and metered fuel and air inputs demonstrated that the coal was being completely burned. Other tests in which theoretical temperature was maintained constant for various levels of CO_2 demonstrated that CO_2 in the oxidizer did not have an

TABLE II
Pulverized fuel compositions

	Colorado	Pittsburgh #8	Western Kentucky	Montana-Powder River region	FMC coal char
Ultimate analysis (%, dry)					
C	73.1	77.2	73.0	67.2	72.8
H	5.1	5.2	5.0	4.4	0.9
N	1.16	1.19	1.40	1.10	.99
S	1.1	2.6	3.1	0.9	3.5
O	9.7	5.9	9.3	14.0	.7
Ash	9.8	7.9	8.2	11.7	21.2
Heating value					
(Btu/lb, wet)	12,400	13,700	12,450	8,900	
(J/g, wet)	28,800	31,800	28,900	20,600	
Proximate analysis (%, wet)					
Volatile	38.9	37.0	36.1	30.5	3.6
Fixed carbon	52.6	54.0	51.2	39.0	73.8
Moisture	3.3	1.2	4.8	21.2	1.8
Ash	8.9	7.8	7.8	9.2	20.8

appreciable chemical effect on NO formation. Comparison between total NO with preheated air as the oxidant and fuel NO with the synthetic mixture as the oxidant was therefore accomplished under nearly identical conditions. Thermal NO is defined as the difference between total NO and fuel NO, on the assumption that thermal fixation of atmospheric nitrogen does not inhibit fuel nitrogen conversion. Data on fuel and thermal NO emissions as a function of stoichiometric ratio are shown in Figure 2, for the Western Kentucky coal for both the divergent and single hole injector. All NO emission data are reduced to zero percent excess O_2; i.e. to stoichiometric air. The divergent injector data on total NO (620°K preheat, 45% swirl, 14% primary air and 21 m/sec (70 ft/sec) throat velocity is consistent in both magnitude and trend with other pilot and full scale data from wall fired units[9] and was reproducible over many months testing. The data clearly show that under these conditions over 80% of the total NO is the result of the oxidation of bound nitrogen in the fuel. Variations in primary air percentage, secondary air swirl and burner throat velocity did
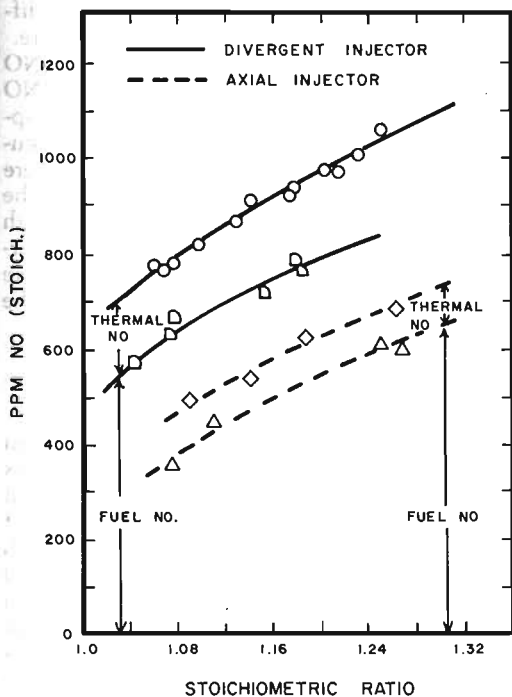

FIG. 2. Total NO and fuel NO emissions: Western Kentucky coal-(620°K preheat, 45% swirl; 14% primary air-divergent injector, 8% primary air-axial injector; 21 m/sec throat velocity)

not change this finding,[9] and under all conditions examined, fuel NO contributed at least 75% of the total NO emissions.

Data from the single hole injector (620°K preheat, 45% swirl, 8% primary air) show that slow mixing drastically lowered total NO emissions. This is in agreement with pilot data[10] and field data on tangentially fired units.[11] However, it is clear that this dramatic reduction was due to a decrease in fuel NO emissions which again comprised approximately 80% of the total. Thus, although a change in mixing significantly altered total emission levels, the dominant NO producing mechanism in all cases was still through fuel nitrogen oxidation.

Although the data shown on Figure 2 are for the Western Kentucky coal they are typical of the results obtained for the Colorado coal, the Pittsburgh coal and the subbituminous Montana coal.[9] In all cases, under typical combustion conditions in our system, fuel NO contributed over 75% of the total NO emissions.

Overall Temperature Dependence

The pulverized coal flames examined in this study were turbulent diffusion flames, with large internal temperature gradients and turbulent fluctuations. In determining the effect of flame temperature, we, therefore, chose the adiabatic flame temperature as the parameter correlating flame temperature, even though the actual bulk gas temperatures were significantly lower. Adiabatic flame temperature was varied from 2100°K to 2600°K by i) changes in secondary "air" preheat, ii) variations of the CO_2 concentration in the inlet "air" iii) introduction of recirculated flue gas in the secondary "air" and iv) slight oxygen enrichment of the inlet "air." Results for the Western Kentucky and the Colorado coals are shown in Figure 3, and are also typical of the other two coals. All the data shown are for 15% excess air and purely aerodynamic variations were minimized insofar as was possible by maintaining the ratio of swirl to axial momentum constant. The data are for the divergent injector and the numbers associated with the data points refer to Table III which describes how each condition was achieved. Total NO emissions increased dramatically with theoretical flame temperature but fuel NO was remarkably insensitive to temperature over a wide range. For the Colorado coal, fuel NO emissions were essentially constant over a theoretical temperature range of 2250°K through 2535°K and a measured wall tempera-
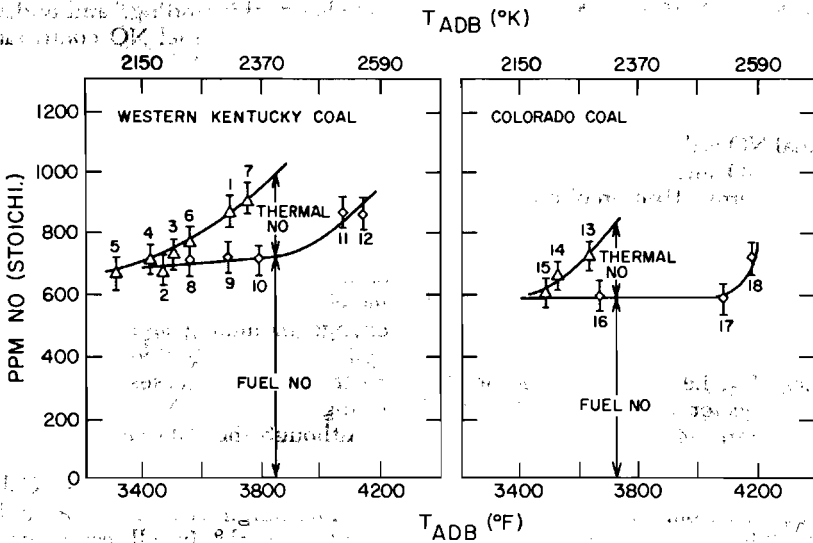
FIG. 3. Temperature dependence of thermal and fuel NO: Western Kentucky and Colorado coals (15% excess air; divergent injector)

TABLE III
Experimental conditions—Figure 3

Western Kentucky coal

1	625°K	(666°F)	preheat (baseline) air
2	315°K	(110°F)	preheat air
3	640°K	(690°F)	preheat air with 10.6% FGR
4	635°K	(685°F)	preheat air with 14.1% FGR
5	645°K	(705°F)	preheat air with 19.0% FGR
6	640°K	(690°F)	preheat 21% O_2, 11.6% CO_2 in N_2
7	555°K	(540°F)	preheat 22.6% O_2 in N_2
8	315°K	(110°F)	preheat 19.3% O_2, 16.0% CO_2
9	315°K	(110°F)	preheat 21.3% O_2, 18.7% CO_2
10	315°K	(110°F)	preheat 21.4% O_2, 11.4% CO_2, in Ar
11	520°K	(475°F)	preheat 21% O_2 in Ar
12	495°K	(435°F)	preheat 23.0% O_2 in Ar

Colorado coal

13	535°K	(505°F)	preheat air
14	540°K	(515°F)	preheat 20.9% O_2, 7.7% CO_2 in N_2
15	550°K	(530°F)	preheat 20.7% O_2, 11.8% CO_2 in N_2
16	375°K	(215°F)	preheat 21% O_2, 18.7% CO_2 in N_2
17	520°K	(475°F)	preheat 21% O_2 in Ar
18	522°K	(481°F)	preheat 23.8% O_2 in Ar

ture range of 1285°K through 1450°K. Above approximately 2550°K, however, fuel NO emissions underwent a sudden increase, and this was observed to occur at a slightly different temperature for each coal shown here.

At low temperatures (2150°K) the total NO emissions approached the (constant) fuel NO value and the thermal NO asymptotically approached zero. Furthermore, within the accuracy of the experiment, the emissions were not dependent on the method for altering the temperature. The Montana and Pittsburgh coals exhibited similar behavior for both thermal and fuel NO over the lower temperature range, but did not allow investigation at the high range due to combustion instabilities.

Coal Composition

Figure 4 is a composite plot of fuel nitrogen conversion to NO data for the three bituminous coals, the subbituminous coal and the coal char, for the two injector types at 545°K preheat and 1.15 stoichiometric ratio. The Pittsburgh and Western Kentucky coals are both high sulfur, eastern bituminous coals. These data indicate that as nitrogen content increases, the corresponding percentage conversion decreases. Consequently actual fuel NO emission levels for the Pittsburgh, Western Kentucky, and also Montana coals with the divergent injector were essentially identical measured either on a dry, corrected volumetric basis (700 ± 15 ppm) or as emission factors (0.82 ± 0.02
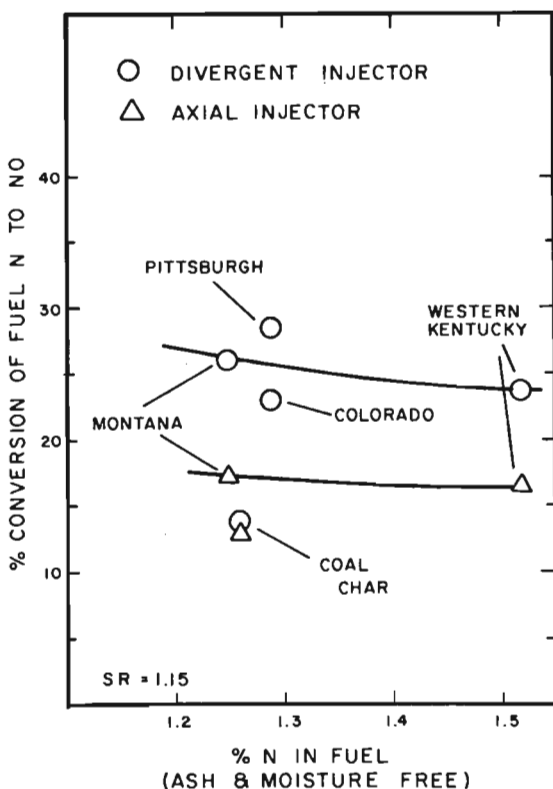
FIG. 4. Effect of pulverized fuel composition (15% excess air, $Ar/O_2/CO_2$ oxidant)

lbs $NO_2/10^6$ Btu, $(3.52 \pm 0.08) \times 10^{-10}$ kg/J).
Figure 4 shows two second order effects which can not be attributed to total nitrogen content and which are outside experimental error. First, comparison of the Western, low-sulfur coals (Colorado and Montana) indicates that coal rank may have a small influence on fuel NO emissions. Second, although the Pittsburgh and Colorado are both bituminous coals with 1.29 percent fuel nitrogen, there is a difference in fuel nitrogen conversion between them. Therefore, coal composition parameters other than coal rank or fuel nitrogen content can have a small but measurable effect.

Slow mixing induced by the axial fuel injector led to lower fuel nitrogen conversions for both coals tested (Western Kentucky and Montana), although the trend with nitrogen content was similar. In marked contrast, coal char gave conversions of 16% which were independent of injector design.

Coal Char

Since the emissions from coal char differed significantly from those of the other coals, the char results are presented in more detail in Figure 5.

Char was burned in two modes: i) the flame mode, in which a turbulent diffusion flame was attached to the injector with the help of a small quantity of methane (20% of the total heat release) in the primary "air" and in which methane simulated nitrogen free volatiles; ii) the reactor mode, in which pure char, without methane, burned far from the injector and which simulated the char burnout regime of coal after all volatiles have been consumed and after significant mixing had taken place. These two modes of char combustion spanned probable conditions during the char burnout regime of pulverized coal combustion, and helped determine the effect of mixing and of "shielding" by residual volatiles[12] on fuel nitrogen conversion to make "char NO."

The char data (corrected for dilution by methane combustion products) show that the influence of combustion mode is small compared to coal; with char the reactor mode emissions were approximately 100 ppm higher than those in the flame mode. It is pertinent to note that when each of the other four coals
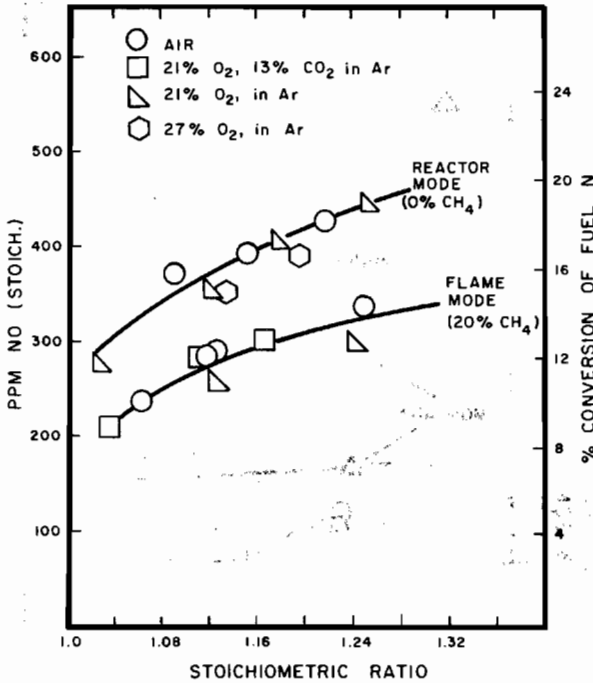
FIG. 5. Total NO and fuel NO emissions from coal char

was burned in the reactor mode, emissions increased by over 1000 ppm, indicating the importance of volatile nitrogen in coal.

Both combustion modes showed the following: i) total NO emissions for char burning in air were low compared to coal, ii) essentially all the emissions were comprised of fuel NO, iii) fuel nitrogen conversion although significant was lower than that of coal, iv) fuel nitrogen conversion was only a weak function of flame temperature.

Discussion

This study lends strong support to the thesis that the dominant NO producing mechanism in practical coal fired units arises through oxidation of chemically bound nitrogen in the fuel. This conclusion is strengthened through the following results: first, our baseline data are consistant in both magnitude and trend with those from field units; second, although fuel nitrogen oxidation was sensitive to changes in injector design, it was always the primary source for NO_x for a wide range of flame types; third, it was impossible to contrive a situation in our system, whereupon fuel nitrogen oxidation comprised less than 75% of the total NO emissions.

Substitution of air by an $Ar/CO_2/O_2$ mixture is a valid means to isolate fuel NO. Furthermore, the difference between total NO and fuel NO is representative of thermal NO, since, as shown on Figure 6, our thermal NO values for coal were in line with those obtained for gas, in this combustor, for the same injectors and under similar aerodynamic and thermal conditions. This indicates that interactions between fuel and thermal NO are not of first order importance.

That fuel NO from pulverized coal combustion is relatively temperature independent over a wide range of flame and wall temperatures indicates that flue gas recirculation (or, indeed, any temperature reduction technique) is of somewhat limited value for NO_x abatement from pulverized coal. Indeed, it appears that without changes in aerodynamics and mixing, there is very little opportunity to lower total NO emissions below the (constant) fuel NO level and still maintain stable flames. It would appear that particle heating rate becomes important only at very high flame (and wall) temperatures and presumably at high initial heat fluxes to the particle, whereupon an increase in fuel nitrogen conversion is observed.

That fuel nitrogen conversion decreased with increasing nitrogen content is in agreement with other data.[2] Coal rank does not
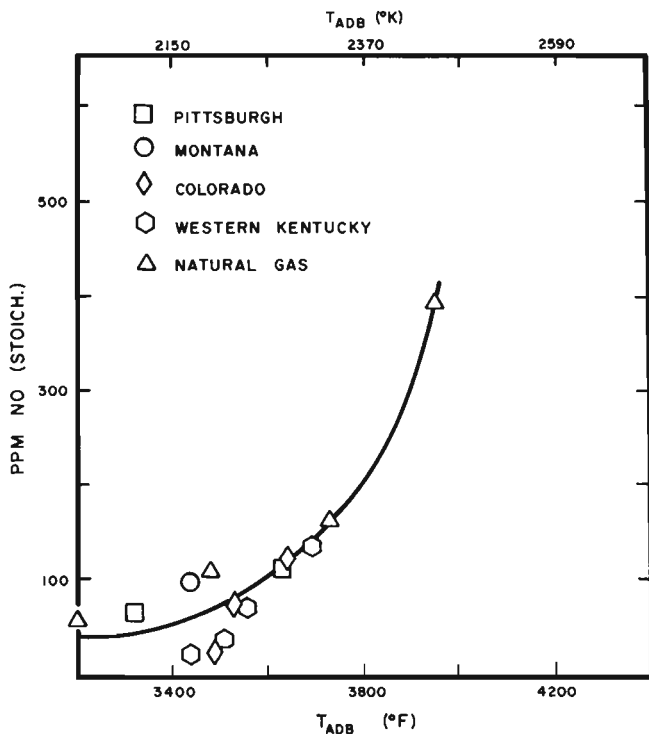
FIG. 6. Thermal NO emissions from coal and natural gas (divergent injector; 15% excess air; 45% swirl)

appear to be a primary variable as far as fuel NO is concerned. The Colorado coal data does not correlate well, and this indicates that factors other than total fuel nitrogen content may be significant when comparing various coals. Further research is necessary to elucidate what these factors are.

The char results have important implications as far as coal combustion is concerned, even though the actual char investigated was not the product of incomplete high temperature coal combustion. Of the nitrogen that goes to the char a sizeable fraction can be converted to NO at high temperatures, but this conversion is less than half of what would be expected from coal combustion. This finding is consistent with theory[7] and other data.[10] In practical systems abatement of "char NO" by combustion modifications, may be difficult since unlike "volatile NO" it is relatively insensitive to changes in early mixing induced by injector design variations. This lends support to the theory that combustion modifications through aerodynamic changes primarily influence "volatile NO," although they may influence the fraction of fuel nitrogen remaining in char. This is consistent with the expectation that

the time scale for conversion of volatile nitrogen is much shorter than the time scale for conversion of char nitrogen. The lack of temperature dependence of char NO is consistent with theories involving diffusion reaction interactions.[7] Further work should entail the combustion of char derived from partial coal combustion, and of chars of various nitrogen contents. It will then be possible to ascertain the potential benefits of altering the volatile and char nitrogen ratio through combustion modifications.

Acknowledgment

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