ELSEVIER

Combustion and Flame 135 (2003) 299–313

Combustion and Flame

The fate of char-N at pulverized coal conditions

Jennifer P. Spinti*, David W. Pershing

Department of Chemical Engineering, University of Utah, Salt Lake City, UT 84112, USA

Received 25 January 2002; received in revised form 12 June 2003; accepted 23 June 2003

Abstract

The fate of char-N (nitrogen removed from the coal matrix during char oxidation) has been widely studied at fluidized bed conditions. This work extends the study of char-N to pulverized coal conditions. Coal chars from five parent coals were prepared and burned in a laboratory-scale pulverized coal combustor in experiments designed to identify the parameters controlling the fate of char-N. The chars were burned with natural gas (to simulate volatiles combustion) in both air and in a nitrogen-free oxidant composed of Ar, CO_2, and O_2. In some experiments, the char flames were doped with various levels of NO or NH_3 to simulate formation of NO_x from volatile-N (nitrogen removed during coal devolatilization). The conversion of char-N to NO_x in chars burned in the nitrogen-free oxidant was 50–60% for lignites and 40–50% for bituminous coals. In char flames doped with NO_x, the apparent conversion of char-N to NO_x (computed using the NO_x measurements made before and after the addition of char to the system) decreased significantly as the level of NO_x doping increased. With 900 ppm NO_x present before the addition of char, apparent conversion of char-N to NO_x was close to 0% for most chars. While there is no clear correlation between nitrogen content of the char and char-N to NO_x conversion at any level of NO_x in the flame, the degree of char burnout within a given family of chars does play a role. Increasing the concentration of O_2 in the system in both air and nitrogen-free oxidant experiments increased the conversion of char-N to NO_x. The effects of temperature on NO_x emissions were different at low (0 ppm) and high (900 ppm) levels of NO_x present in the flame before char addition.

Keywords: Pulverized coal combustion; Char nitrogen; NO_x formation

---

1. Introduction

The abundance of coal as an energy source is offset by the negative environmental impacts associated with coal combustion such as the emission of nitrogen oxides (NO_x), which are both acid rain precursors and contributors to photochemical smog. The establishment of much stricter NO_x emissions limits for coal-fired power plants has led to a renewed interest in the mechanisms by which NO_x forms in pulverized coal (pc) flames. Studies have shown that over 75% of the NO_x present in pc flames results from the oxidation of nitrogen in the coal matrix, also known as fuel-N [1]. The remainder comes from thermal-NO_x and prompt-NO_x formation mechanisms [2].

The fate of fuel-N is determined by the fate of its component parts, volatile-N (removed during coal devolatilization) and char-N (removed during char oxidation). Experimental data suggest that differences may exist between the fates of volatile-N and of char-N. Pershing and Wendt [1] estimated that during pulverized char combustion, the char-N conversion to NO was 12 to 16%; during pulverized coal combustion at the same conditions, the overall fuel-N conversion to NO was 28%. Similar results were obtained by Brown and Thomas [3], who compared

---

* Corresponding author. Tel.: +1-801-562-1446; fax: +1-801-585-1456.

E-mail address: spinti@crsim.utah.edu (J.P. Spinti).

0010-2180/03/$ – see front matter
doi:10.1016/S0010-2180(03)00168-8

the temperature-programmed gasification in 20% O_2 (balance Ar) of 6 coals of varying rank and of the chars produced from the coals. The fraction of nitrogen converted to NO for the coals was usually equal to or higher than for the chars. Song et al. [4] also reported that the conversion of char-N to NO_x was lower than the corresponding value for fuel-N in their experiments with coal and char particles in an electrically heated furnace. Finally, Davidson [5] stated that the fate of char-N may be more important than that of volatile-N because of the capability of aerodynamic abatement of NO_x formation from volatile-N.

Much of the work related to the fate of char-N has been done at fluidized bed combustion (FBC) conditions: temperatures of ~1050-1150K and particle diameters in the mm range. A review article by Johnsson [6] tabulates available FBC data on the fractional conversions of char-N to NO and N_2O. The conversions of char-N to NO vary between 20-80%, largely because of wide variations in experimental techniques and the influence of devolatilization temperature, combustion temperature, coal type, O_2 concentration, particle size, and nitrogen content of the char. Harding et al. [7] studied the release of NO during the combustion of coal chars at temperatures between 823–1323K in relation to coal and char structural characterization parameters. Chars with low surface areas and reactivities tended to have higher levels of char-N to NO conversion, as did the high-rank coal chars at lower combustion temperatures, where the reaction was under chemical control. This relationship between char reactivity and char-N conversion to NO was also noted in a study by Wang et al. [8], where data from the temperature-programmed combustion of chars indicated that char-N conversion to NO decreased with increasing reactivity of the char. They did comment, however, that char-N to NO conversion varied by a factor of 2 over a relatively narrow range of reactivity, indicating the importance of other factors.

The goal of this work was to extend the study of char-N to pc conditions. Coal chars were both prepared and subsequently burned at pc conditions in a series of experiments designed to determine the important parameters influencing the fate of char-N in pc flames.

2. Experimental Methods

A bench scale test facility at the University of Utah, the U furnace, was used for this study. This multifuel combustion research facility, shown in Fig. 1, has a U configuration and is down-fired with a nominal firing rate of 29 kW. The combustion chamber is approximately 0.16 m in diameter and the overall length is 7.3 m. The composite walls of the furnace include both refractory and insulation board layers to minimize heat loss. The combustion chamber is accessed through opposing ports located along the entire furnace length.

The U furnace is equipped with a premixed burner mounted on the top left-hand side of the combustor. The burner (see Fig. 2) consists of five main sections. The first section includes inlets for the secondary air and the primary air/coal (or char) mixture, which are forced through holes in a mixing plate. The two streams impinge on each other approximately 2.5 cm below the mixing plate in the second section of the burner, the mixing chamber. The third section of the burner, the radiation shield, prevents premature ignition of the fuel/oxidant mixture in the mixing chamber. Natural gas injection occurs in the fourth section of the burner through 18-2.4 mm holes equally spaced around the diameter of the gas injection ring. The fifth section, a transition piece from the burner into the furnace, is refractory-lined. A quarl, although not shown in Fig. 2, extends from the bottom of the burner down into the combustor. The quarl has an ID of 6.3 cm at the top and opens to the diameter of the combustor over a length of 20.3 cm.

Five coals of various rank were selected for this study: (1) Illinois #6, a high-volatile C bituminous coal; (2) Pittsburgh #8, a high-volatile A bituminous coal; (3) Utah, a high-volatile bituminous coal from the Huntington Canyon mine in Utah; (4) Knife River, a North Dakota lignite; (5) Black Thunder, a Powder River Basin subbituminous coal. All coals were pulverized to a standard power plant grind of at least 70% through −200 mesh. Coal chars were prepared from these 5 parent coals by feeding coal to the U furnace via the premixed burner and then collecting the partially oxidized coal from the first port in the furnace (located 30 cm below the quarl).

The char collection system is shown in Fig. 3. The entire cross section of the furnace was covered with a piece of insulation board inserted into the port opposite the port from which the particle-laden gases were extracted. A stainless steel quench gas injector was inserted into the same port as the insulation board. Air or N_2 was fed into the quench gas injector for the purpose of diluting and quenching the furnace flow as it exited through the opposite port. A secondary form of quenching, used during some of the char collection experiments in conjunction with air quenching, consisted of an air-atomized water spray nozzle mounted at the exit port. Upon exiting the furnace port, the quenched, particle-laden gases entered a water-cooled assembly where temperatures were further reduced. Downstream of this cooling assembly was a cyclone designed to remove particles

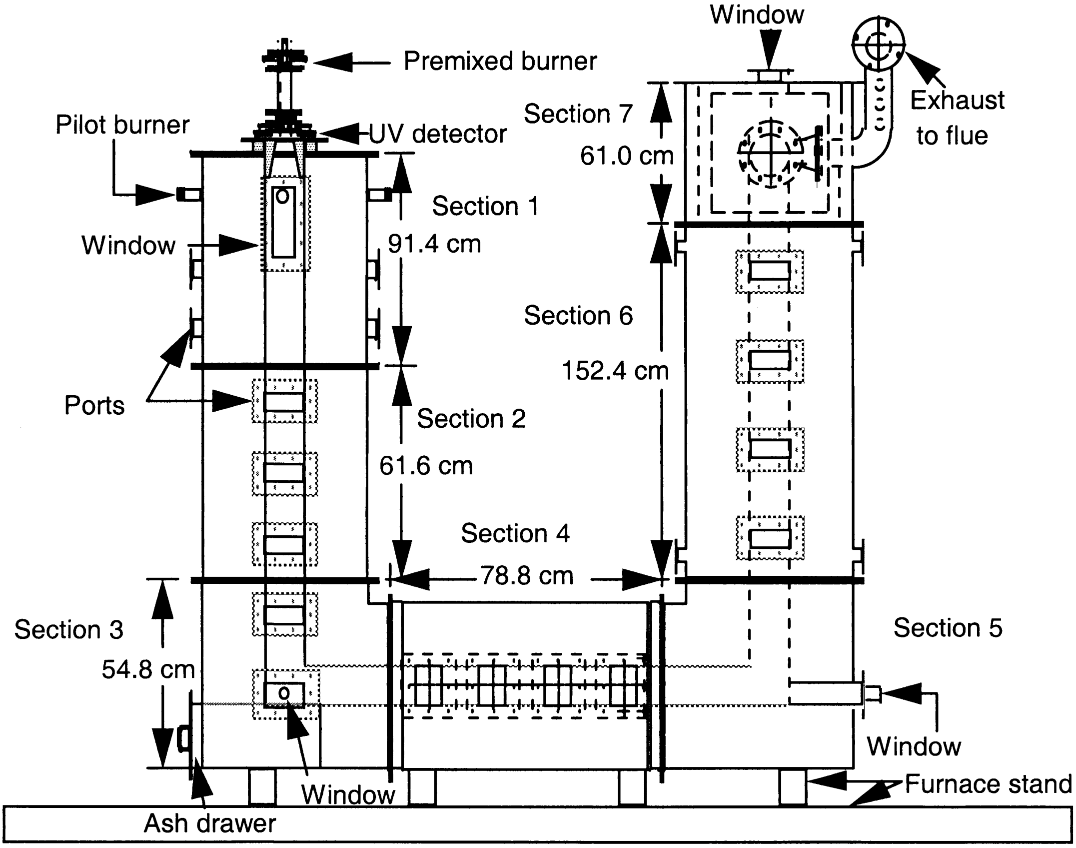

Fig. 1. Multifuel, refractory-lined test furnace at the University of Utah. Overall length of the furnace is 7.3 m and the nominal firing rate is 29 kW.

larger than 50 m in diameter with an efficiency of 99.99% and particles of diameter 10 m with 96% efficiency. In practice, removal efficiencies varied from 60 to 80%. Downstream of the cyclone, an air-atomized water spray nozzle further cooled the gases before their entering the vacuum pump.

During char collection, the stoichiometric ratio in the flame zone was maintained at approximately 1.15. Coal firing rates were varied from 22-32 kW with most falling in the range of 22–26.4 kW. Electric heaters were used to preheat the secondary combustion air to 500K. Based on limited suction pyrometer flame temperature measurements in the first furnace port below the flame, the temperatures at which char was prepared varied from ~1700–1820K.

Chars from the same parent coal which were quenched by the same method and had similar burnout levels were combined and mixed well. All char mixtures were subsequently identified by the parent coal and by the dates of char collection included in that mixture, that is, Pitt (25,26,29 Sept). Analyses were performed on samples from each char mixture; results for all chars are found in Table 1. The computed burnout, based on the carbon and ash content of the parent coal and of the collected char, is also shown.

The collected chars were subsequently burned with natural gas, a fuel mixture referred to as simulated coal. The purpose for firing the char in combination with the natural gas was twofold. One, without an additional fuel source, the char flame was difficult to ignite and sustain. Two, combustion of the natural gas simulated volatiles combustion with the advantage that natural gas was a nitrogen-free fuel. Tests requiring the elimination of all nitrogen sources except char-N were conducted in a nitrogen-free oxidant mixture of $Ar/CO_2/O_2$. All mixtures noted in this paper refer to volume percent of each component. If a quantifiable gas phase NO_x source was needed for a particular experiment, the simulated coal was doped with either NH_3 or NO.

Flame temperatures in the simulated coal flames exceeded the temperatures at which the char was

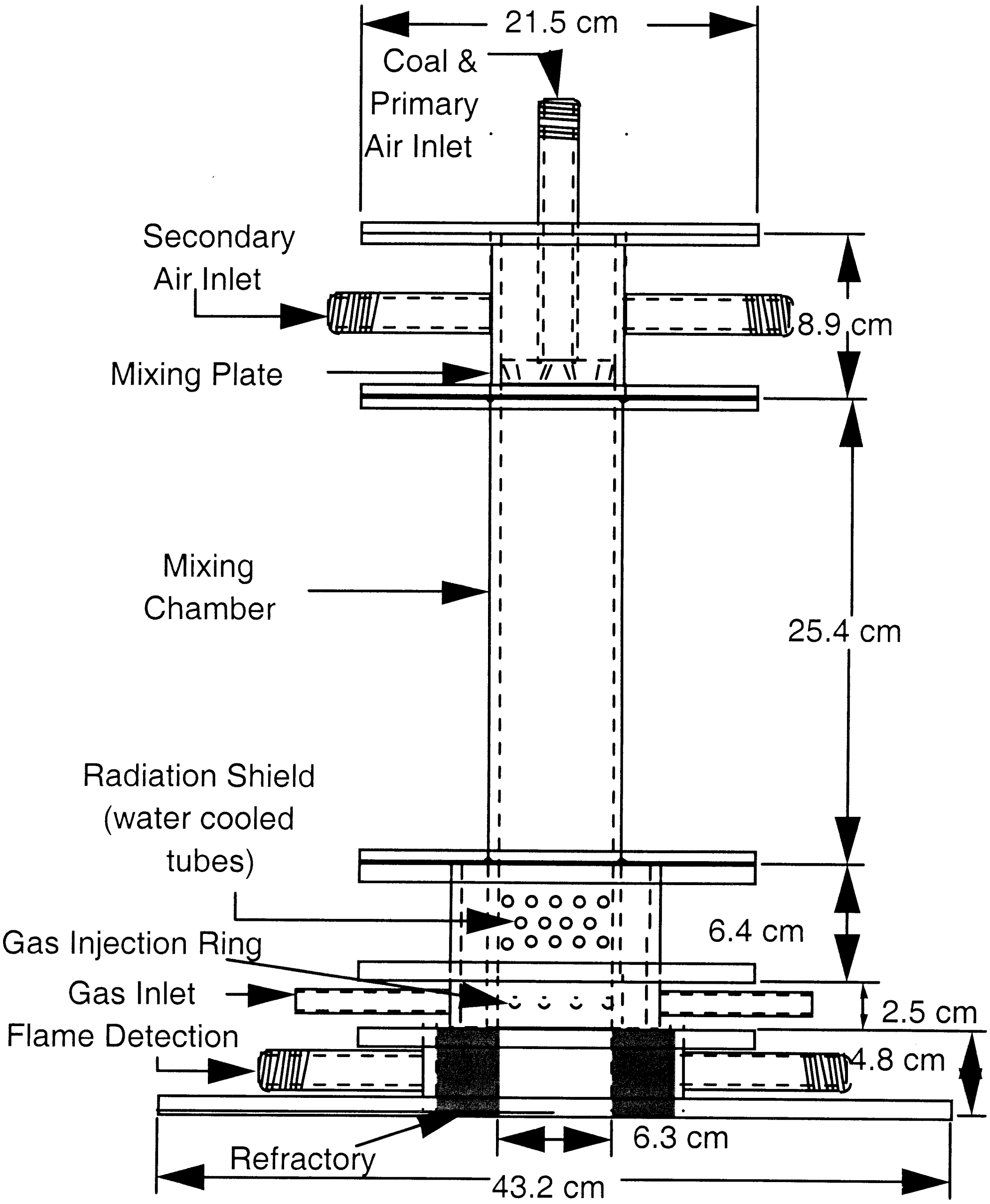

Fig. 2. Premixed burner mounted on the U furnace. Coal, char and/or natural gas can be fired as fuels.

prepared by 100–200K. Hence, there is a slight possibility that residual volatile-N remained in some of the chars and was subsequently devolatilized in the simulated coal flame. Because of the high degree of burnout of all the chars and the scale of these experiments, any NO_x resulting from residual volatile-N is estimated to be in the noise of the data.

Unless otherwise indicated, the simulated coal experiments were conducted with preheated combustion air at an overall stoichiometric ratio of 1.15 (3% excess O_2) with natural gas and char firing rates of 24.9 kW and 4.4 kW respectively. At these conditions, temperatures in the burner's mixing chamber ranged from 490–530K. Char burnout as measured by excess O_2 concentration was nearly complete by the first port in the furnace and exceeded 99% at the furnace exhaust.

Samples were withdrawn from the furnace exhaust using either a quartz probe or a stainless steel, water-cooled probe. A heated Teflon line connected

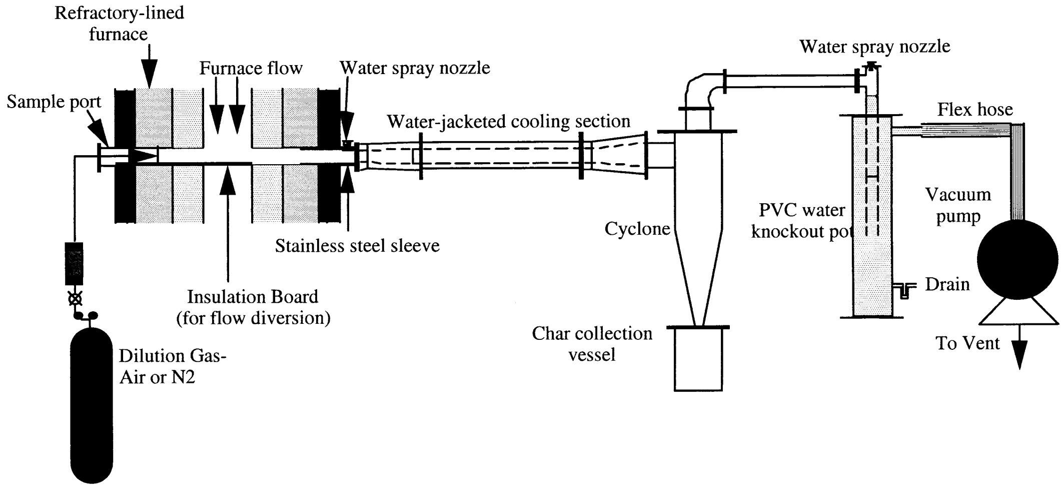

Fig. 3. System used to collect char from a port in the U furnace.

to the probe was maintained at a temperature slightly above 373K. From the Teflon line, the sample passed through a heated quartz glass cyclone followed by a heated Teflon filter. The clean gases were then dried in a series of two Permapure ion-exchange membrane dryers.

At each experimental condition, a gas sample was analyzed by an NDIR CO/CO_2 analyzer, a zirconia oxide O_2 analyzer, and a chemiluminescent NO_x analyzer (i.e., TECO), for a period of three minutes; all reported data represent a three minute average. Another gas sample was sent to a Nicolet FT-IR for additional analysis of NO_x species' concentrations (NO, NO_2, and N_2O). NO_x concentrations measured by the TECO were compared to those measured by the FT-IR. A signal suppression problem was observed with TECO NO_x measurements made when burning simulated coal in nitrogen-free oxidant due

Table 1
Char proximate and ultimate analysis data[a]

Sample name	Moisture (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulfur (%)	Ash (%)	Calorific value (kJ/kg)	Computed % burnout
Pitt #8 (25, 26, 29 Sept)	0.96	60.96	0.72	1	1.04	0.41	35.53	9178	81.61%
Pitt #8 (27, 28, 29 Sept)	1.05	68.08	0.7	1.14	2.4	0.48	26.91	10387	72.89%
Pitt #8 (19, 24 Oct)	2.89	65.44	0.48	1.06	0.33	0.62	31.14	9484	77.48%
Ill #6 (14, 19, 20, 21 Sept)	1.01	65	0.52	1.13	0.05	0.4	32.61	9518	85.39%
Ill #6 (18 Sept)	0.89	75.95	1.21	1.61	2.71	0.51	17.85	11451	68.81%
Ill #6 (22 Sept)	1.2	70.3	0.56	1.28	0.05	0.41	27.57	10227	81.31%
Ill #6 (12, 13 Oct)	0.7	63.03	0.49	1.12	0.05	0.46	34.89	9101	86.76%
Ill #6 (16 Oct)	0.7	70.65	0.69	1.13	0.05	0.51	27.34	10301	81.06%
Utah (13 Sept)	1.27	65.64	0.71	1.14	0.05	0.37	34.07	9393	78.72%
Knife River (26 Oct)	2.77	47.31	0.44	0.46	0.05	1.58	49.36	6592	86.62%
Knife River (29, 30 Oct)	1.13	51.23	0.66	0.64	1.93	1.62	43.42	7656	83.53%
Knife River (31 Oct, 1 Nov)	2.05	51.58	0.77	0.51	2.85	1.39	42.02	7718	82.86%
Black Thunder	0.88	40.12	0.43	0.48	1.68	0.62	56.17	5960	94.75%

[a] C, H, N, S, & O reported on a dried sample basis. Other data are reported on an as received sample basis.

primarily to the presence of argon in the oxidant [9]. The FT-IR consistently measured NO_x concentrations that were 15–20% higher than what the TECO measured. For this reason, all NO_x data reported in this paper are from the FT-IR.

3. Results

3.1. Computing conversion of char-N to NO_x

The y-axis for most of the data plotted in this paper reads either "Apparent % Conversion of Char-N to NO_x" or "% Conversion of Char-N to NO_x." The latter is only used for experiments run in nitrogen-free oxidant with no NH_3 or NO doping. The only source of nitrogen in the system is the char-N, so there is no ambiguity as to the source of the NO_x. Computed conversions from these experiments are hereafter referred to as inherent conversions. In all other experiments, additional sources of nitrogen exist, so conversion is only apparent. The apparent conversion is based on the incremental change in measured NO_x, either positive or negative, that results when char is added to a natural gas flame.

Determining the apparent char-N to NO_x conversion at each experimental condition requires two data points: (1) the gas phase NO_x concentration when no char is present and (2) the gas phase NO_x concentration after char is added to the system. Hence, the first step was to fire natural gas with the combustion air required for the gas/char flame at the desired stoichiometric ratio and then to measure the NO_x concentration. The second step was to add char to the system and measure the NO_x concentration again. Based on these two measurements, an apparent char-N to NO_x conversion was computed using the formula given below.

$$Conversion: = \frac{((NO_{x,gas/char} - NO_{x,gas})/10^6) \times Q_{dry} \times MV}{F_{dry} \times N_{dry} \times MW_N} \qquad (1)$$

In Eq. 1,

Conversion = Apparent percent conversion of char-N to NO_x

NO_x,gas/char = NO_x measured when firing simulated coal (e.g., char/gas mixture)

NO_x,gas = NO_x measured when firing natural gas before the addition of char

Q_{dry} = Total dry furnace flow rate (calculated) for the simulated coal

MV = Molar volume of NO_x gases at standard conditions

F_{dry} = Char feed rate (dry basis)

N_{dry} = Weight percent nitrogen in the char (dry basis)

MW_N = Molecular weight of N.

Inherent conversion is computed using the same formula with the exception that "NO_x, gas" is 0 ppm since char-N is the only source of nitrogen in the system.

3.2. Baseline NO_x production levels from char-N

To establish baseline levels of NO_x production from char-N, the suite of chars was burned in a nitrogen-free oxidant consisting of 15 mole % CO_2, 21 mole % O_2, and the balance Ar. This experimental configuration represents the limiting case where NO_x formation from volatile-N is 0 ppm. The experimental data are plotted in Fig. 4 as a function of carbon to nitrogen mass ratio in the char (C_C/C_N). Some points represent repeat tests with the same char. The inherent char-N to NO_x conversion levels are in the range of 40-60% and are clustered together within each parent coal grouping. In general, the char-N to NO_x conversions of the lower rank coal chars are higher than those of the three bituminous coal chars.

In an experiment at FBC conditions, Ninomiya et al. [10] burned char particles in an Ar/O_2 atmosphere. The conversion of char-N to NO for two coal chars increased linearly on a double-logarithmic scale with an increase in C_C/C_N. Conversions were in the range of 40–90%. Although the present data do not show the same linear dependency, the conversions levels are in the same range.

In early work by Pershing and Wendt, coal char was burned with small amounts of methane in a laboratory scale furnace, yielding char-N to NO_x conversions of less than 20% [11]. However, the coal char was prepared by a high temperature gasification process and may not be similar to the char produced in a pc flame. Chen et al. also reported char-N to NO conversions of less than 20% when burning a coal char with propane in an Ar/25% O_2 mixture [12]. Other researchers have reported results in the range shown in Fig. 4. De Soete reported fractional conversions of char-N to NO in the 0.35 to 0.67 range for highly devolatilized bituminous coal chars burned in an Ar/O_2 mixture in a fixed bed reactor [13]. Shimizu et al. pyrolyzed nine coals in a fluidized bed and then burned the char in an Ar/13.5% O_2 mixture in a fixed bed reactor [14]; fractional char-N to NO_x conversions of 0.2–0.5 were measured. Finally, Wang et al. prepared char from a high-volatile bituminous coal by heating the coal to 1773K and then burned the

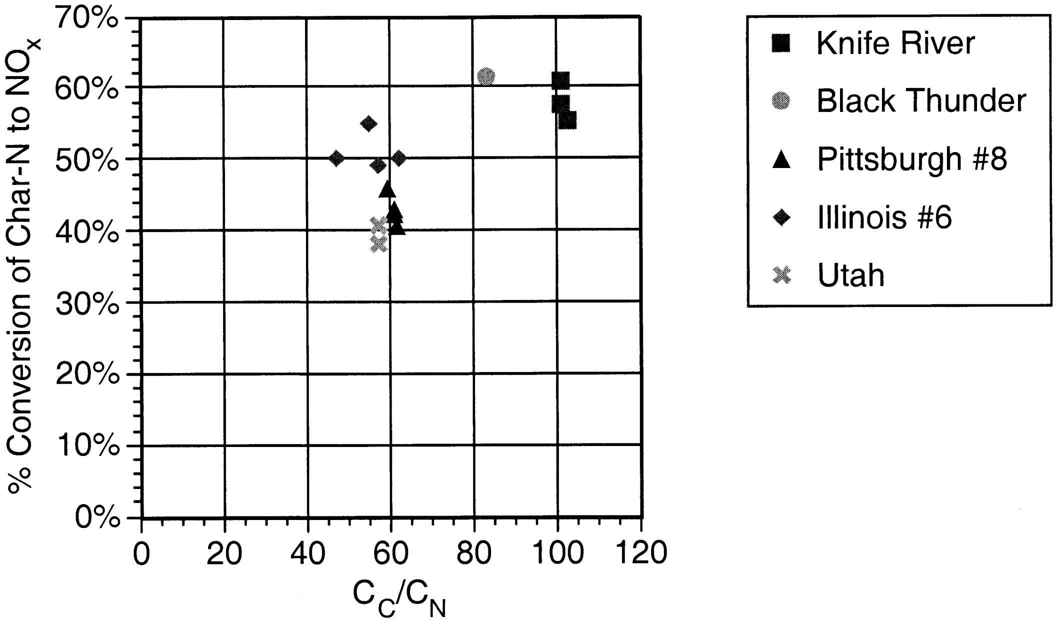

Fig. 4. Conversion of char-N to NO_x for various coal chars as a function of carbon to nitrogen mass ratio in the char. The oxidant is $64\%Ar/15\%CO_2/21\%O_2$.

char in an Ar/20% O_2 mixture [15]. Fractional conversion of char-N to NO was 0.49. Fractional conversions for other chars prepared at lower temperatures were much lower.

Figure 4 indicates that there is a wide variation in char-N to NO_x conversion for chars with similar $C_C/_CN$ ratios. Hahn and Shadman [16] provide an explanation for this variation and for the large conversions of char-N to NO_x in the absence of NO in the free stream. They use NO formation and reduction reactions coupled with a detailed pore structure model to show that overall NO conversion is influenced as much by structural changes and pore diffusion as chemical kinetics. Particles undergo changes in size and density and develop non-uniform internal area distributions. All heterogeneous reactions are affected by these structural changes, including the NO formation and reduction reactions. Using their model, Hahn and Shadman predict char-N to NO conversions of ~20% for a char particle burning in a furnace with lower heating rates and lower temperatures than those found in pc combustion.

3.3. *Effect of initial gas phase NO_x concentration*

In any actual coal flame, there will be some NO_x present in the gas phase before the onset of char oxidation because of thermal NO_x, prompt NO_x, and NO_x formation from volatile-N. In the present char-N experiments, NO_x concentrations from 0–900 ppm were measured when firing natural gas alone or natural gas doped with NO or NH_3. This NO_x concentration is subsequently referred to as the initial or free stream NO_x concentration, that is, the level of NO_x the char will be exposed to when it begins to burn.

The effect of the initial NO_x concentration on the apparent conversion of char-N to NO_x was studied with all of the coal chars. Results are plotted in Fig. 5 for the series of chars prepared from Pittsburgh #8, Knife River, and Black Thunder coals. The data points at 0 ppm initial NO_x were obtained by burning the simulated coal in artificial oxidant. The data centered around 150 ppm initial NO_x were obtained by burning the simulated coal in air, so those NO_x levels are the result of thermal NO_x formation. The data points at higher initial NO_x levels were obtained by doping the flames with either NO or NH_3. Also included on Fig. 5 is the nitrogen content of each char on a dry basis. Similar results are plotted in Fig. 6 for the chars of Illinois #6 coal. In both figures, multiple data points were taken at some test conditions.

The apparent conversion of char-N to NO_x is a strong function of the initial NO_x concentration for all chars, regardless of rank and nitrogen content. As the initial NO_x rises, apparent conversion decreases dramatically as increasing amounts of NO_x (or NO_x precursors) are reduced to N_2. Furthermore, at high initial NO_x levels, a large quantity of NO_x is reduced

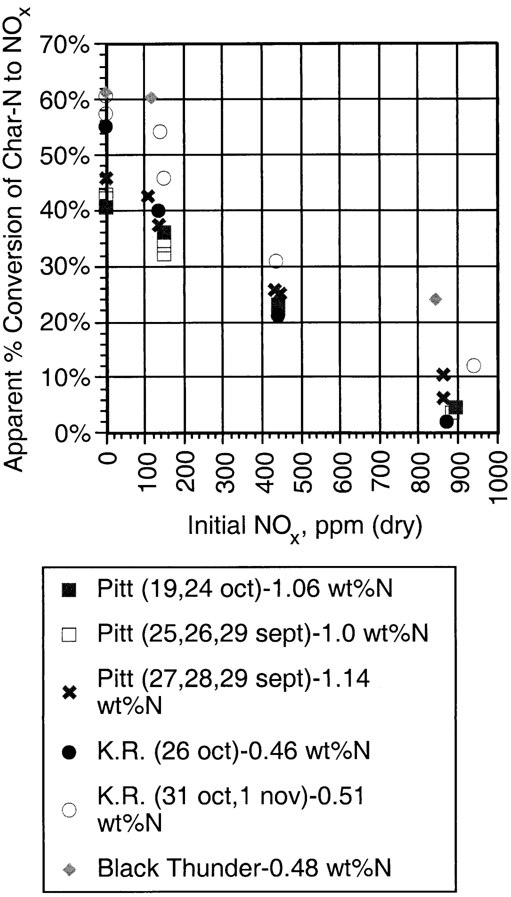

Fig. 5. Effect of initial gas phase NO_x concentration on char-N to NO_x conversion for Pittsburgh #8, Knife River, and Black Thunder coal chars.

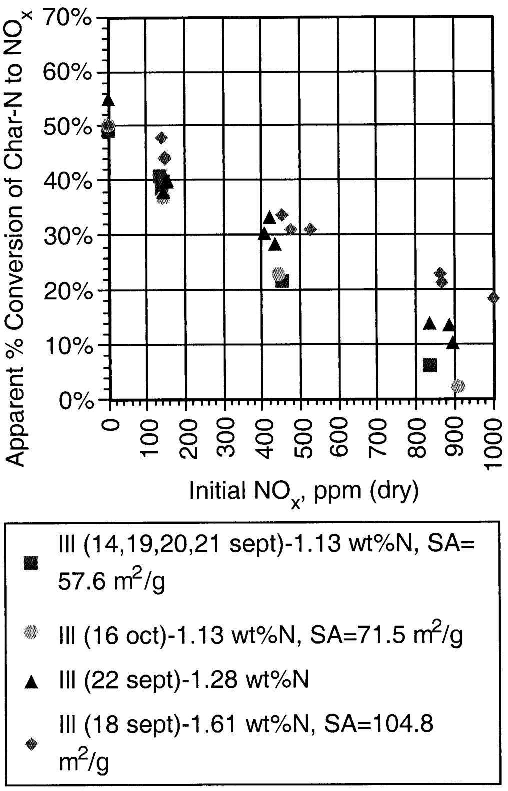

Fig. 6. Effect of initial gas phase NO_x concentration on char-N to NO_x conversion for Illinois #6 coal chars with varying nitrogen content.

to N_2. Consider the apparent char-N to NO_x conversion of 22.4% obtained with Pitt (25,26,29 Sept) char at an initial NO_x level of 438 ppm; 77.6% of the char-N, the equivalent of 289 ppm NO_x in the gas phase, is reduced to N_2.

Because the trend in Fig. 5 and Fig. 6 is the same for all chars, these results suggest that the controlling NO_x formation and reduction reactions are insensitive to coal rank. This observation has been corroborated by Shimizu et al. [14] at FBC conditions. Based on char experiments and results from a single particle model, they concluded that the intrinsic reactivity of char to NO is essentially the same for all chars. They attributed the differences in char-N to NO conversion for various chars to differences in internal surface area. Wang et al. [8] inferred char reactivity toward NO from its reactivity toward O_2 and then concluded that char-N to NO conversion decreased with increasing reactivity of the char. Nevertheless, the scatter in the data for less reactive chars indicated that temperature and structural variations also influenced their results.

The effect of initial NO concentration on NO conversion efficiency was modeled by Visona and Stanmore using a single particle model [17]. The model predicted that, for a lignite char, conversion of char-N to NO decreased linearly with increasing external NO. This dependency was expected since the NO reduction term in the model increased linearly with NO partial pressure. The nearly linear results for all chars in Fig. 5 and Fig. 6 support the use of this model for NO reduction on the char surface.

In Fig. 5, there is not a clear correlation between nitrogen content of the char and char-N to NO_x conversion at any of the initial NO_x concentrations tested. However, for the chars of a given parent coal (Pittsburgh #8 or Knife River), there is a general trend of increasing char-N to NO_x conversion with increasing char-N content. This trend is also observed for the Illinois #6 coal chars in Fig. 6 and is most pronounced at the highest initial NO_x level (850-900 ppm).

In work that yielded similar results, Wang et al.

studied a much wider range of US and UK coal chars in an entrained flow reactor and found no clear relation between char-N to NO conversion and the nitrogen content (dry basis) of the char when the free stream NO concentration was 0 ppm [8]. The chars in the study were prepared from pulverized coal by pyrolosis at 1000°C; heating rates were similar to those present during pc combustion.

Using a simple film model, Wendt and Schulze [18] predicted that the conversion of char-N to NO decreased with increasing nitrogen content of the char (0 ppm NO in the free stream). This result was obtained because the NO formation reaction was linear with respect to nitrogen content while the NO reduction mechanism (a homogeneous reaction) was second order with respect to NO. However, Wendt and Schulze did not include a heterogeneous NO reduction mechanism in their model, which has already been shown to be important in the present work.

The correlation between char-N content and char-N to NO_x conversion for chars from the same parent coal can be explained by first considering the degree of burnout of each of the chars in Table 1. For any set of chars from the same parent coal, nitrogen content decreases as burnout increases. This result is expected because nitrogen is usually assumed to oxidize in the proportion it is found in the char matrix. Next, the fact that the apparent char-N to NO_x conversion at high initial NO_x levels decreases as char burnout increases indicates that the char/NO reduction reaction is not limited by available surface sites. Instead, this trend emphasizes the importance of pore structure and diffusion in the latter stages of burnout. As burnout increases, pores are enlarged and walls between neighboring pores collapse, reducing the surface area available for reaction but increasing the diffusivity of the gas species, NO and O_2 [16]. As char burnout increases, NO in the free stream more readily diffuses into the pores, where it is reduced on the char surface. The result is that when two different chars from the same parent coal are burned with the same free stream NO_x concentration, the more highly burned out char (with lower char-N content) reduces more of the gas phase NO_x and its apparent char-N to NO_x conversion is less.

At some point, the NO/char reduction reaction will be limited by the high ash content of the pore matrix, which may explain why the Black Thunder char data in Fig. 5 are consistently higher than those of any other char, even Knife River which has a similar nitrogen content. The Black Thunder char had a higher degree of burnout than the other chars (see Table 1). In addition, the Black Thunder char particles were smaller than the other char samples (48% smaller than 38 m compared to 20–34% for the other chars). According to Visona and Stanmore, as particle size decreases, char-N to NO conversion increases because the regime of diffusion control becomes more pronounced [17]. Less O_2 is able to penetrate the particle, so less NO is formed in the particle. The NO that is formed is near the pore mouth, so it diffuses out before reduction on the char can occur.

As suggested by Shimizu et al. [14], internal surface area could also play a role. N_2 BET surface areas were measured for three of the Illinois #6 chars in Fig. 6. For these chars, the surface areas differ by less than a factor of two. The two chars with equal nitrogen content, Ill (14,19,20,21 Sept) and Ill (16 Oct), have surface areas of 57.6 m2/g and 71.5 m2/g, respectively, but there is no appreciable difference between the two sets of data. The char with higher nitrogen content and higher char-N to NO_x conversion, Ill (18 Sept), also has the highest surface area. Hence, the effect of internal surface area is difficult to evaluate with the present data set. In addition, N_2 BET measurements may be low compared to CO_2 measurements [19]. Visona and Stanmore [17] conducted a sensitivity analysis of char-N to NO conversion on internal surface area (0 ppm NO_x in the free stream). Increasing the internal area by an order of magnitude left char-N to NO conversion at 1750K unchanged. Perhaps pore structure is more important than total internal area because it is pore structure that affects species' diffusivities.

3.4. *Effect of O_2 concentration on char-N to NO_x conversion*

Because coal char is consumed primarily by oxidation reactions, it seems logical that O_2 concentration would play a significant role in char-N conversion to NO_x. Hence, a study was conducted by burning simulated coals in artificial oxidant ($Ar/CO_2/O_2$) at various excess O_2 levels.

Results from Pittsburgh #8 and Illinois #6 coal char experiments are plotted in Fig. 7 as conversion of char-N to NO_x versus excess O_2 measured in the exhaust. For both chars tested, inherent char-N to NO_x conversion increases slightly with increasing excess O_2. Song et al. observed a similar trend burning a lignite char at 1750K [4]. The char was prepared at 1750K from a 44 m pulverized coal. Char-N to NO_x conversion increased from 5% to 30% as the fuel/oxygen equivalence ratio was decreased from 3 to 0.2. An opposite trend was observed in the single-particle fluidized bed experiments of Tullin et al. [20] and Goel et al. [21]. As O_2 concentration was raised, NO yields fell and N_2O yields rose. Because N_2O would be rapidly destroyed to form N_2 at the pc conditions in the present experiments, a rise in N_2O

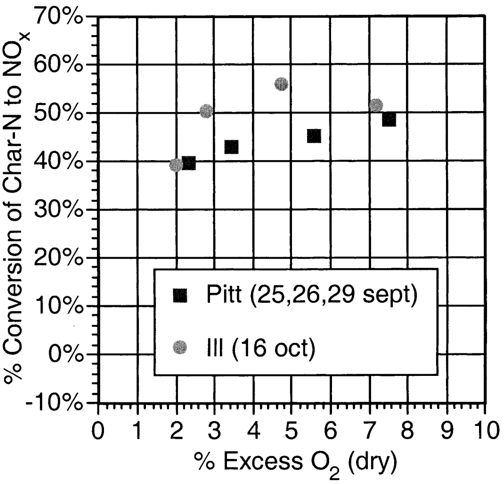

Fig. 7. Effect of excess O_2 on conversion of char-N to NO_x. The oxidant is 64%Ar/15%CO_2/21%O_2.

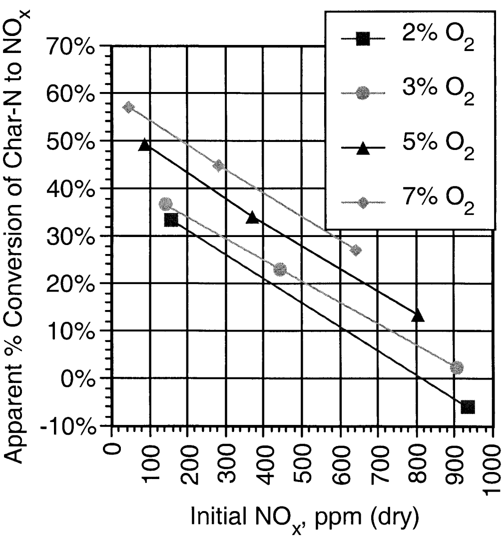

Fig. 8. Comparison of the effects of excess O_2 and of initial gas phase NO_x concentration on the conversion of char-N to NO_x for an Illinois #6 coal char.

yields at high O_2 concentrations would result in a drop in char-N to NO_x conversion, exactly opposite of the trend seen here.

Several explanations exist for this difference in trends. First, in the experiments of Tullin et al. and Goel et al., single particles in the millimeter size range were combusted at FBC conditions. In contrast, micron-sized particles in a particle cloud were combusted at pc conditions in the present experiments. Second, the FBC experiments were conducted in an environment free of H_2O vapor while the present experiments were conducted in an H_2O-rich environment due to the simultaneous combustion of natural gas and char. Because H_2O has been proposed as a reactant in the release of char-N, the lack of H_2O vapor may have affected the FBC char-N oxidation mechanism, and thus the role of O_2 in char-N to NO_x conversion.

Visona and Stanmore model the effect of free stream O_2 concentration on char-N to NO conversion efficiency for a 38 (m lignite char particle burning at 1750K, conditions that more closely match the present experiment [17]. They note an increase in conversion of 14% when the O_2 concentration is increased from 2% to 20%; above 20% O_2 in the free stream, the conversion appears to plateau. This small increase in conversion is comparable to the increase seen in Fig. 7. Reducing the free stream O_2 concentration changes the char-N to NO_x conversion by reducing the rate of nitrogen oxidation in the char. In the Visona and Stanmore model, the nitrogen oxidation rate is linearly dependent on O_2 partial pressure.

Because excess O_2 concentration and initial NO_x level both impact the fate of char-N, measurements were taken at various initial NO_x concentrations at each of four excess O_2 levels (2%, 3%, 5%, and 7%) using Ill (16 Oct) char. The data are plotted in Fig. 8. The percent conversion was highest for the 7% excess O_2 case and lowest for the 2% excess O_2 case. The negative conversion indicates that NO_x levels actually decreased when char was added to the system. The parallel lines at constant excess O_2 indicate that the primary effect of O_2 is on the oxidation of char-N.

In the range of free stream NO_x and O_2 concentrations tested, NO_x concentration in the free stream has a greater effect than O_2 concentration on char-N to NO_x conversion. Again, these effects are predicted by the Visona and Stanmore model. For a 38 m lignite char particle burning at 1250K, char-N to NO conversion is reduced from 95% to 45% when the free stream NO concentration is increased from 0–1400 ppm, while conversion increases by 14% when O_2 concentration increases from 2% to 20% [17]. The data in Fig. 8 indicate that an accurate kinetic rate for NO reduction on char is more important than the char-N oxidation rate in determining NO_x emissions from char.

3.5. *Influence of flame temperature at various initial NO_x levels*

The impact of local flame temperature on inherent char-N oxidation was studied by varying the amount of CO_2 in the artificial oxidant mixture from 25–0%; O_2 concentration was held constant at 21% and Ar

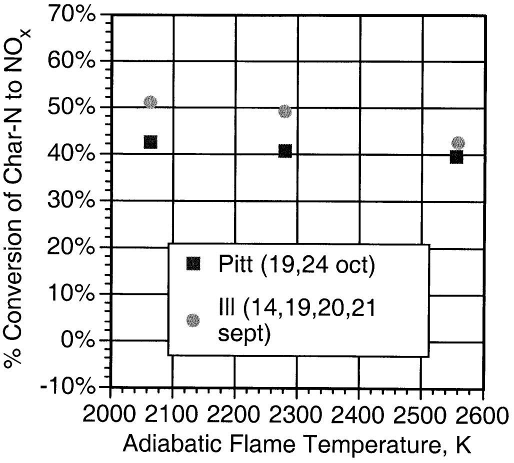

Fig. 9. Influence of flame temperature on char-N to NO_x conversion. The oxidant is $Ar/CO_2/21\%O_2$ with CO_2 varied from 0 to 25% and Ar making up the difference.

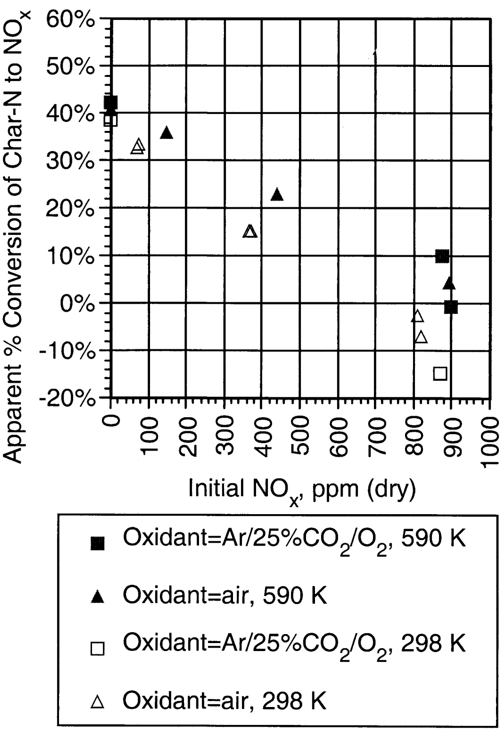

Fig. 10. Comparison of the effects of flame temperature and of initial gas phase NO_x concentration on the conversion of char-N to NO_x for a Pittsburgh #8 coal char.

made up the balance. Computed adiabatic flame temperatures for this range of CO_2 concentrations were approximately 2060K to 2560K. Data from two chars, Pitt (19,24 Oct) and Ill (14,19,20,21 Sept), are shown in Fig. 9 as a function of adiabatic flame temperature. Conversion decreases slightly with increasing adiabatic flame temperature for both chars. A strong flame temperature dependence would indicate a reaction rate-controlled process; the small flame temperature dependencies in Fig. 9 suggest a diffusion-controlled process. Hahn and Shadman note the importance of diffusion in their single particle model [16]. They show profiles of O_2 and NO in a particle during the second stage of particle combustion when NO formation and reduction rates are high because of high temperatures and high O_2 and NO concentrations. They conclude: (1) that the concentration profiles and structural properties are mutually dependent and (2) that the structural properties cannot be ignored when modeling the fate of char-N since most of the NO is formed during this second stage.

The data are reported using computed adiabatic flame temperatures rather than actual flame temperatures for two reasons. First, actual flame temperatures were measured with fine wire, type B thermocouples sheathed in ceramic tubing for protection. These thermocouples were inserted to the furnace centerline in ports along the length of the furnace. Unfortunately, ash and slag buildup coupled with radiation losses from the ceramic sheath introduced large errors. To quantify the errors, comparison measurements were made with a suction pyrometer in a natural gas flame with preheated air (adiabatic flame temperature = 2400K). In the first port below the burner, the sheathed thermocouples measured low by ~200–250K with the suction pyrometer consistently measuring temperatures of ~1920–1975K. Unfortunately, the suction pyrometer was too fragile to use regularly. Second, the large thermal load of the furnace walls means that wall temperature fluctuations are small relative to flame temperature fluctuations. These tests were run in rapid succession, so the temperature in the local flame zone was changing rapidly compared to the wall temperature, another contributor to thermocouple measurement error. The use of adiabatic flame temperature in Fig. 9 illustrates the local flame temperature differences introduced by changing CO_2 concentration in the oxidant.

To quantify the impact of temperature on the char/NO reduction step, experiments were run with Pitt (19, 24 Oct) char at initial NO_x levels which varied from 0-900 ppm; data were collected both in artificial oxidant (25% CO_2 in the mixture) and in air. Local flame temperatures were varied by reducing the air preheat from 590K to 298K. This reduction in air preheat decreased flame temperatures by approximately 100K.

As seen in Fig. 10, there is only a slight effect of temperature at 0 ppm initial NO_x (in agreement with

Fig. 9). At all other initial NO_x levels, the apparent conversions of char-N to NO_x with no air preheat (298K) are several percent lower than conversions with air preheat (590K). At the 900 ppm initial NO_x level, the char-N to NO_x conversions with no air preheat are negative, which means a significant fraction of the initial NO_x is being reduced to N_2.

From the standpoint of reducing NO_x formation in coal flames, these data indicate that at NO_x levels typically found in the late char burnout regime (200–500 ppm), cooler temperatures are preferable. The fact that apparent char-N to NO_x conversion is more temperature sensitive as the initial NO_x level increases suggests that the char/NO reduction step(s) is more temperature sensitive than the char-N oxidation step. Visona and Stanmore examine the temperature sensitivity of both the oxidation and reduction reactions with their single particle model [17]. For char-N oxidation, the concentration of NO in the pores increases from 500 ppm to 2300 ppm when the temperature is raised from 1250–1500K; char/NO reduction is turned off. However, the temperature dependence decreases dramatically between 1500K and 1750K when the maximum pore NO concentration increases from 2300 ppm to 2400 ppm, and these temperatures are closer to the temperature range explored in the present work. For the char/NO reduction reaction, they compare the kinetics of Levy et al. [22] and Chan et al. [23] at 1250K, 1500K and 1750K; char-N oxidation is turned off. The Levy reaction shows much stronger temperature sensitivity between 1500K and 1750K ($\Delta NO_x = 500$ ppm) than between 1250K and 1500K ($\Delta NO_x = 200$ ppm), consistent with the present experimental observations. Unfortunately, they do not show any data for the Chan reaction at 1500K, but the ($\Delta NO_x = 700$ ppm between 1250K and 1750K.

3.6. The fate of fuel-N in the parent coals

For comparison, the fate of fuel-N was determined experimentally with four of the parent coals of chars used in this study: Pittsburgh #8, Utah, Illinois #6, and Knife River. The coal firing rate was 29.3 kW, the overall stoichiometric ratio was 1.15, and the oxidant was a mixture of Ar, CO_2 (15% by volume), and O_2. Figure 11 summarizes these data and compares them to data from Pershing et al. [24], which were taken from a wide range of coals (lignites to anthracites) burned in an artificial oxidant mixture of Ar, CO_2, and O_2 in a 21 kW furnace mounted with a premixed burner. The present coal data fall within the range of data reported by Pershing et al. The Pershing data set exhibits a slight decrease in fuel-N conversion to NO_x with increasing fuel-N while the present data show a trend similar to that seen with the coal chars, i.e. a small increase in fuel-N conversion to NO_x with increasing fuel-N content. These differences highlight the variability inherent in this type of experiment and the importance of separating the effects of NO_x formation from char-N and volatile-N.

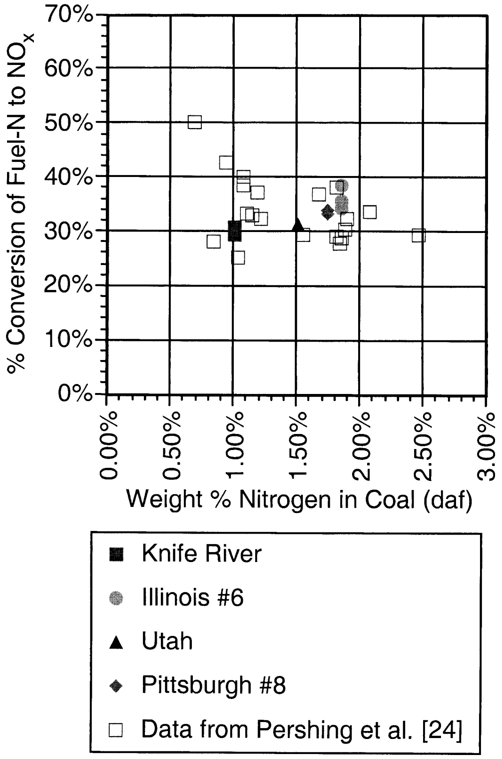

Fig. 11. Conversion of fuel-N to NO_x in the parent coals. The oxidant is $64\%Ar/15\%CO_2/21\%O_2$.

The actual NO_x concentrations measured for the four coals ranged from 750 to 1200 ppm. At comparable levels of free stream NO_x in the char experiments (see Fig. 5 and Fig. 6), char-N to NO_x conversions were in the range of 0 to 25%, lower than the 30 to 40% range for fuel-N conversion to NO_x seen in Fig. 11 for the coals. Hence, the conversion rate of volatile-N to NO_x is greater than that of char-N to NO_x, an observation made by other researchers [25].

4. Discussion

4.1. Application of results to entire char oxidation process

The degree of burnout in the chars collected for this study ranged from 68 to 87%, which implies the latter stages of char oxidation. The work of Hurt and

Davis [26] has shown that there are two distinct stages during the char burnout process. First is the rapid, high-temperature stage which ends with a near-extinction of heterogeneous reactions because of the loss of global particle reactivity when approximately 70% of the char carbon has been consumed. Second is the final burnout stage which occurs slowly and at lower temperatures.

Although the chars in this study were collected close to the near-extinction event, the remaining discussion assumes that the results apply throughout the char oxidation process.

4.2. Minimization of overall NO_x formation

The lowest conversion levels of char-N to NO_x were seen at high initial NO_x levels, low excess air levels, and no air preheat. However, a high initial NO_x level translates to a high conversion of volatile-N to NO_x. If the conversion of volatile-N to NO_x is reduced by designing a burner with a fuel-rich core, the conversion of char-N to NO_x will increase unless the char/volatile nitrogen split (i.e., the fraction of nitrogen that remains in the char versus the fraction that is devolatilized) is altered.

In principle, a burner designer can manipulate four fundamental parameters to minimize overall fuel-N emissions: (1) volatile-N oxidation, (2) char/volatile nitrogen split, (3) char-N oxidation, and (4) reduction of volatile (and thermal) NO during the char oxidation process. The results of this study can be used to optimize these parameters to minimize overall NO_x emissions.

To illustrate this concept, three scenarios were considered for Illinois #6 coal char. In one scenario, 50% of the nitrogen originally present in the coal was assumed to remain in the char; in the other two scenarios, this number was 40% and 30% respectively. For each of the three scenarios, total NO_x production (NO_x from both volatile-N and char-N) was computed for various conversions of volatile-N to NO_x. Char-N to NO_x conversions for the computations were obtained from experimental Ill (22 Sept) char data. The results of these computations are plotted in Fig. 12.

Three conclusions can be drawn from Fig. 12. First, the lowest overall NO_x production is achieved at low levels of volatile-N to NO_x conversion for all three levels of nitrogen content in the char. Second, the global minimum for NO_x production is reached by devolatilizing as much nitrogen as possible and then reducing NO_x formation from volatile-N to extremely low levels, not by manipulating char-N to NO_x conversion. Third, accurate modeling of NO_x production from a pc flame requires reliable predictions of the nitrogen partitioning between volatiles and char in addition to correct volatile-N and char-N reaction models.

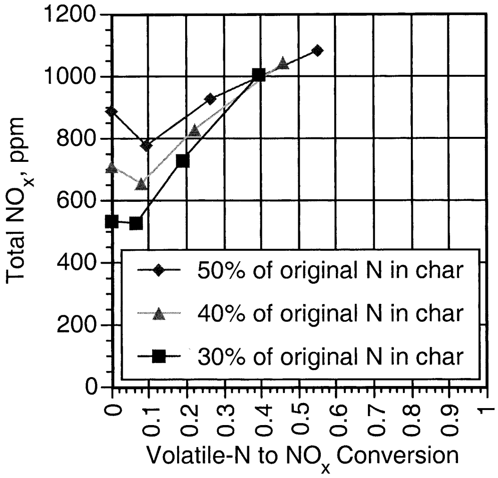

Fig. 12. Estimated NO_x emissions from Illinois #6 coal.

4.3. Low-NO_x burner/boiler design

A low-NO_x burner/boiler design based on the conclusions from the present char-N data might include the following: a fuel-rich flame core for minimizing the conversion of volatile-N to NO_x, high temperatures during devolatilization for maximum removal of nitrogen from the coal matrix, a char oxidation zone with temperatures as cool as possible (using flue gas recirculation, high heat removal by the boiler walls, or some other technique) and with low excess O_2 concentrations, and a boiler volume which can accommodate the longer residence times required for complete char burnout at lower temperatures. Of course, there are limits to how low the excess O_2 levels in the boiler can be maintained because of concerns of too much residual carbon in the ash.

The present char-N data indicate a finite limit to the lowest NO_x levels achievable through flame zone combustion modifications. If NO_x formation from volatile-N can be reduced to 0 ppm, char-N conversion to NO_x is still significant. Conversely, apparent NO_x formation from char-N can be reduced to 0 ppm, but only at the price of a high gas phase NO_x concentration from volatile-N. Hence, it appears that NO_x concentrations cannot be reduced to levels approaching 0 ppm without the use of downstream NO_x reduction techniques such as reburning, SNCR, or SCR.

5. Conclusions

The fate of char-N in pc flames has been determined experimentally for chars from five parent coals that were produced and subsequently oxidized at pc conditions. The results of this study are summarized below.

- Inherent char-N conversion to NO_x (oxidation of char-N in the absence of gas phase NO_x) is high (50–60% with low rank coals and 40–50% with bituminous coals) under typical pc combustion conditions.
- Apparent char-N conversion to NO_x (char-N oxidation/reduction plus the reduction of previously formed NO_x) decreases significantly as the initial NO_x level rises, that is, from 45% conversion with no initial NO_x to near 0% conversion with 900 ppm initial NO_x for the Pittsburgh bituminous coal. This effect is observed with lignite, subbituminous and bituminous coals, indicating the dependency of the char/NO reduction rate on the NO concentration in the pores.
- When all the chars are considered together, there is not a clear correlation between char-N content and char-N to NO_x conversion at any of the initial NO_x levels tested. Within a set of chars from the same parent coal, there is a general trend of increasing conversion with increasing char-N content at all initial NO_x levels that is explained by considering the degree of burnout of the char.
- Both inherent and apparent conversions to NO_x increase with increasing excess air in about equal proportions, suggesting that the primary effect of increasing O_2 is to increase the rate of char-N oxidation.
- The initial (or free stream) NO_x concentration had a greater effect on the char-N to NO_x conversion than the O_2 concentration, demonstrating the importance of an accurate kinetic rate for NO reduction on char.
- Inherent conversion to NO_x decreases slightly with increasing local temperature while apparent conversion to NO_x at high initial NO_x levels increases with temperature. These trends suggest that the char/NO reduction step is more temperature sensitive than the char-N oxidation step at pc conditions.
- Because of the inverse relationship between char-N conversion and the level of NO_x formed from volatile-N, it will be difficult to achieve very low NO_x emissions from pulverized coal combustion without (1) almost complete devolatilization of the fuel-N or (2) downstream NO_x reduction methods such as reburning or SNCR.

Acknowledgments

This work was supported by the Department of Energy under Project No. DEFG2294PC94223 with Project Officer Tony Mayne. We would like to thank Mr. Dana Overacker for his help in running the laboratory facilities.

References

[1] D.W. Pershing, J.O.L. Wendt, Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1976, p. 389.
[2] J.A. Miller, C.T. Bowman, Prog. Energy Combust. Sci. 15 (1989) 287–338.
[3] S.D. Brown, K.M. Thomas, Fuel 72 (1993) 359–365.
[4] Y.H. Song, J.H. Pohl, J.M. Beer, A.F. Sarofim, Combust. Sci. Technol. 28 (1982) 31–39.
[5] R.M. Davidson, Perspectives-Nitrogen in Coal, IEA Coal Research Report No. IEAPER/08, 1994.
[6] J.E. Johnsson, Fuel 73 (1994) 1398–1415.
[7] A.W. Harding, S.D. Brown, K.M. Thomas, Combust. Flame 107 (1996) 336–350.
[8] W. Wang, S.D. Brown, C.J. Hindmarsh, K.M. Thomas, Fuel 73 (1994) 1381–1388.
[9] J.P. Spinti, Ph.D. dissertation, University of Utah, Salt Lake City, UT, 1997.
[10] Y. Ninomiya, K. Yokoi, N. Arai, M. Hasatani, Int. Chem. Eng. 29 (1989) 512–516.
[11] D.W. Pershing, J.O.L. Wendt, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 60–67.
[12] S.L. Chen, M.P. Heap, D.W. Pershing, G.B. Martin, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1982, p. 1271.
[13] G.G. de Soete, Twenty-Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1990, p. 1257.
[14] T. Shimizu, Y. Sazawa, T. Adschiri, T. Furusawa, Fuel 71 (1992) 361–365.
[15] W.X. Wang, K.M. Thomas, H.Y. Cai, D.R. Dugwell, R. Kandiyoti, Energy Fuels 10 (1996) 409–416.
[16] W.A. Hahn, F. Shadman, Combust. Sci. Technol. 30 (1983) 89–104.
[17] S.P. Visona, B.R. Stanmore, Combust. Flame 106 (1996) 207–218.
[18] J.O.L. Wendt, O.E. Schulze, AIChE J. 22 (1996) 102–110.
[19] J.L. Johnson, in: M. A. Elliot (Ed), Chemistry of Coal Utilization 2nd Supplementary Volume, Wiley, New York, 1981 p. 1523.
[20] C.J. Tullin, A.F. Sarofim, J.M. Beer, J. Inst. Energy 66 (1993) 207–215.
[21] S.K. Goel, A. Morihara, C.J. Tullin, A.F. Sarofim, Twenty-Fifth Symposium (International) on Combus-

tion, The Combustion Institute, Pittsburgh, 1994, p. 1051.
[22] J.M. Levy, L.K. Chan, A.F. Sarofim, J.M. Beer, Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1996, p. 3205.
[23] L.K. Chan, A.F. Sarofim, J.M. Beer, Combust. Flame 52 (1983) 37–45.
[24] D.W. Pershing, M.P. Heap, S.L. Chen, Pulverized Coal Combustion: Pollutant Formation and Control, 1970–1980, U.S. Environmental Protection Agency Report No. EPA-600/8-90-049, Chapter 9, 1990.
[25] S.L. Chen, M.P. Heap, D.W. Pershing, G.B. Martin, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1982, p. 1271.
[26] R.H. Hurt, K.A. Davis, Twenty-Fifth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1994, p. 561.