Advanced Combustor Design Concept to Control NO_x and Air Toxics

Final Technical Report

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1.0 Executive Summary

Direct coal combustion needs to be a primary energy source for the electric utility industry and for heavy manufacturing during the next several decades because of the availability and economic advantage of coal relative to other fuels and because of the time required to produce major market penetration in the energy field. However, the major obstacle to coal utilization is a set of ever-tightening environmental regulations at both the federal and local level. It is, therefore, critical that fundamental research be conducted to support the development of low-emission, high-efficiency pulverized coal power systems.

The objective of this program was to develop fundamental understanding regarding the impact of fuel and combustion changes on NO_x formation, carbon burnout and air toxic emissions from pulverized coal (pc) combustion. During pc combustion, nitrogen in the coal can be oxidized to form nitrogen oxides (NO_x). The 1990 Clean Air Act Amendments established much stricter NO_x emissions limits for new and existing coal-fired plants, so there has been renewed interest in the processes by which NO_x forms in pc flames. One of the least understood aspects of NO_x formation from pc combustion is the process by which char-N (nitrogen remaining in the char after devolatilization) forms either NO_x or N₂, and the development of a fundamental understanding of this process was a major focus of this research.

The overall objective of this program was to improve the ability of combustion system designers and boiler manufacturers to build high efficiency, low emission pulverized coal systems by improving the design tools available to the industry. The specific program goals were to:

- Use laboratory experiments and modeling to develop fundamental understanding for a new submodel for char nitrogen oxidation (a critical piece usually neglected in most NO_x models.)
- Use existing bench scale facilities to investigate alternative schemes to stabilize slowly mixed flames which have the potential of producing ultra-low NO_x levels with high carbon burnout. Also characterize the air toxic emissions from these flames.
- Develop new char nitrogen model for use with a comprehensive combustion model that can be applied to the design and analysis of new and existing boilers.

Experiments were conducted in the University of Utah U furnace, a refractory-lined combustion research facility with a nominal firing rate of 29 kW and a combustion chamber diameter of 16 cm. The U furnace was equipped with a premixed burner to ensure a well-mixed, uniform flame. Coal chars were prepared by firing the U furnace with pulverized coal and then collecting the partially-oxidized coal from a port near the burner. Chars were collected from three bituminous, one subbituminous, and one lignite coal. A commercially-obtained char made from coconut shells was added to the experimental matrix.

The chars were subsequently burned in a simulated coal flame consisting of natural gas (to simulate coal volatiles) and coal char; NH₃ or NO was also used in some tests to simulate NO_x formation from volatile-N. These simulated flames served a dual purpose: one, to study the fate of char-N at pc conditions and two, to effectively separate the fate of char-N from the fate of volatile-N.

Parametric studies with the coal chars revealed that the amount of NO_x present in the gas phase when the char began to burn (referred to as initial NO_x) had a greater effect on char-N to NO_x conversion than any other parameter tested; conversion decreased sharply with increasing initial NO_x concentration. These data suggest a lower limit to the minimum achievable NO_x levels from char-N since char-N to NO_x conversion decreases at the expense of increasing conversion of volatile-N to NO_x (i.e., initial NO_x). In other parametric studies, the effect of increasing O₂ concentration was to increase char-N conversion to NO_x while the effect of reducing furnace temperatures was to decrease char-N to NO_x conversion at all initial NO_x levels except 0 ppm.

Tests with the commercially-obtained char suggest that NO reduction on char carbon is not the most significant source of NO_x reduction during char oxidation. The release of char-N as HCN followed by the homogeneous reactions of HCN to form NO and N₂ and the reaction of NO with char-N to form N₂O must also be considered. The char-N data in this study also show that the accurate prediction of NO_x formation from char-N depends on the accurate modeling of the nitrogen partitioning between volatile-N and char-N.

An analytical solution of a simple single particle model for the char-N conversion to NO was developed. This model was in agreement to with previous modeling work and with general experimental observations.

Model predictions were compared to results presented in this report on the combustion of char in a furnace at PC conditions. The model predicted in a satisfactory way the char-N conversion to NO at low NO bulk concentration. However at high NO bulk concentration, the model underpredicts char-N conversion to NO. Additional research will be needed to resolve these discrepancies. The model presented herein with the fitted NO reduction kinetics obtained from the experimental work can be used in CFD codes for NO prediction. The present results suggest that the value of K_{NO} is a function of NO conversion and this variation can be built into the model. Additional data will be needed to better establish the functionality and the mechanism for the changing coefficient with conversion.

A series of experiments was also conducted to measure the fly ash mass and elemental composition as a function of particle size under five different pulverized coal combustion conditions. The motivation was to investigate the effect of various combustion modifications for NO_x reduction on the partitioning of metals to the PM_{2.5} and PM₁ particulate emissions. As expected, based on previous studies, the metals analysis showed enrichment of volatile elements in the smallest particle size flyash size fraction. Because of the natural size distribution of coal fly ash, the mass collected for the PM₁-enriched fraction was very small. The concentrations of many elements in the fine particles were near the limits of detection and there was poor agreement between the duplicate samples taken at the same combustion condition. There were

no clear trends in metals vaporization between the five combustion conditions. Differences, if present, were small which indicates that increased emissions of toxic metals are not a major concern for the NO_x control conditions tested.

2.0 Preliminary Screening Studies - NO_x Formation From An All-Axial Multifuel Burner

2.1 Introduction

According to the United States Department of Energy (DOE), coal usage in the U. S. will double by 2030 despite conservation efforts and renewable energy growth. This increase, coupled with the increasingly stringent emissions limits prescribed by the 1990 Clean Air Act Amendments, demands that U.S. electric utilities and heavy industries build more efficient and environmentally safe coal-fired power plants. As a consequence, the DOE initiated programs to promote the utilization of recent technological developments in NO_x control, material science, and computer interfacing for the design and operation of advanced, combined-cycle, coal-fired power generation systems.

Figure 2-1 illustrates one such combined cycle which consists of twin high-temperature combustor/air heater (HITAF) units, one gas turbine, and a steam turbine producing an overall plant output of 268 MW. The combustor (HITAF) is used to preheat clean, pressurized air (the working heat transfer fluid) through both radiative and convective heat exchangers. Because of the novel radiant heat exchanger design required by the demand for a high temperature working fluid, the combustor is operated with hot, running slag walls. After exiting the HITAF at 1255 K, the pressurized air is further heated to the turbine inlet temperature of 1644 K by a gas-fired duct burner. The turbine exhaust has a vitiated oxygen (O₂) concentration of about 17.6% due to the presence of combustion products from the duct burner. Part of this vitiated stream is used as combustion air in the HITAF with the remainder being passed through a steam cycle. The flue gas from the HITAF is also passed through the steam cycle for heat removal.

The goal of the experiments described in this introduction was to evaluate near burner combustion modification alternatives for controlling the NO_x emissions in a hot-walled furnace (similar to the HITAF configuration) to ultra low levels. In conventional pulverized coal flames, up to 80% of the NO_x formed is from nitrogen bound in the coal matrix, also known as fuel-N (Pershing and Wendt, 1975). The other large source of NO_x is thermal NO_x, which results from the fixation of molecular nitrogen (N₂) at high temperatures. Since thermodynamics favors the reduction of NO_x and fuel-N to N₂ under O₂ deficient furnace conditions, net NO_x production is greatly affected by combustion modifications (Song et al., 1981b). Combustion modification techniques such as staged combustion (Crawford et al., 1975; Wendt et al., 1979; Song et al., 1981b) and reburning (Wendt et al., 1973; Kremer and Schulz, 1986; Chen et al., 1989; Mereb and Wendt, 1990) have been widely researched and successfully implemented for NO_x reduction. These techniques exploit the fact that both NO_x precursors and NO_x are reduced to N₂ in a fuel-rich environment.

Notwithstanding the success of these combustion modification techniques, an understanding of the dynamics of NO_x production in the near burner region is critical to attaining ultra low NO_x levels through combustion modifications. Several investigators have studied near burner aerodynamics and the burner configurations required for low NO_x production (Heap et al., 1976;

Figure 2-1. Simplified schematic of an advanced, combined-cycle, coal-fired power generation system.

Folsom et al., 1983; Smart and Weber, 1989; Abbas et al. 1991; Azuhata et al., 1990). Most operate on the principle of creating a large, fuel-rich zone in the near burner region followed by slow mixing of additional oxidant, often with heavy cooling. Data from these investigations has led to the design, fabrication and successful implementation of low-NO_x burners for industrial applications (Bowman, 1992).

Another combustion alternative which affects the near burner region is the cofiring of pulverized coal and natural gas. Gas cofiring has been used in full scale, coal-fired utility boilers (Vejtasa, 1992) where relatively modest NO_x reductions (less than 10%) have been achieved; results depend on cofiring configuration and amount of gas used. Despite this full scale

application of gas cofiring, bench scale data are very limited. One group of investigators has published a study of stability limits of pulverized fuels burned with natural gas support (Milosavljevic, 1990). Hence, the focus of this work is on the combined effects of gas cofiring with other near burner combustion modification techniques on NO_x formation in a hot-walled furnace.

2.2 Experimental Facility

In order to evaluate the proposed low-NO_x concepts, experiments were performed using a new bench scale test facility located at the University of Utah. This 29 kW, refractory-lined combustion research facility is described in detail in Appendix A; a simplified drawing of the facility is shown in Figure 2-2. It has a “U” configuration and is down-fired. The combustion chamber is 0.16 meters in diameter and 7.3 meters in length with composite refractory walls to minimize heat losses. To simulate a hot-walled system, the furnace was built with no wall heat removal other than normal conduction. Under typical coal-fired operating conditions with the all-axial burner, the slag on the furnace walls was molten throughout the entire left vertical tower of the furnace. The all-axial burner, shown in Figure 2-3, is mounted on the top left side of the U furnace. Access ports are located along the entire length of the furnace. The facility has the option of using electrically-preheated combustion air and/or high temperature vitiated air from a gas-fired hot gas generator. The hot gas generator is located on the floor directly above the U furnace; its use is explained in “Vitiated Oxidant” on page 19.

The all-axial burner is designed to produce a naturally staged, axial jet flame with a fuel-rich center core. The burner (Figure 2-3) consists of three concentric tubes through which the coal/primary air, natural gas and secondary air streams enter the combustion chamber. The coal-laden primary air stream (unheated) enters through the middle tube. The cofiring fuel, natural gas, is injected through an annular ring around the coal/air jet. A removable insert containing eight axial holes (0.19 cm diameter) can be placed in the annular ring so that the gas exits in discrete jets. Unless otherwise indicated, experiments were performed with the insert in the annular ring. This annular gas stream will henceforth be referred to as stabilization gas because its use insures that the ignition front is stable on the fuel injector. The secondary air (heated) enters the combustion chamber through an annular ring around the outside of the stabilization gas annulus. The burner is equipped with both axial and swirl air inlets for the secondary air; in these experiments the axial inlets were used except where otherwise noted. The refractory quarl attached to the base plate of the burner is 20.3 cm in length and opens from a diameter of 5.2 cm at the top to 15.2 cm at the bottom.

Exhaust gas samples were withdrawn through a water-jacketed stainless steel probe, then filtered and dried. Samples were analyzed for NO (chemiluminescence), O₂ (paramagnetic), CO₂ (NDIR), and CO (NDIR). Reported gas concentrations are time-averaged over one minute and adjusted to a basis of 3% excess O₂. CO concentrations in all experiments never exceeded 60 ppm and usually were below 20 ppm.

LOI and soot formation were not measured in these experiments because they are, in general, very low in this refractory tunnel furnace where mixing only has to occur across a

Figure 2-2. Experimental refractory-lined combustion research facility with hot gas generator.

Figure 2-3. Drawing of the multifuel burner with cutaway views of the injector tip.

furnace diameter of 0.16 m and where downstream temperatures are high enough that running slag is found on the walls 1.8 m below the burner.

The coal used in this study, a Utah high volatile bituminous coal, was obtained in two shipments. A proximate and an ultimate analysis as well as a particle size distribution were obtained on the coal from each shipment. The tabulated results are shown in Table 2-1, Table 2-2, and Table 2-3; all results are given as weight percent. In Table 2-2, DAF means the data are given on a dry, ash free basis; also, oxygen content was obtained by difference. Overall excess air measured at the furnace exit was $3\% \pm 0.5\%$ for all experiments.

Table 2-1. Proximate analyses of two shipments of a Utah coal.

	Moisture (%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)	Calorific Value (kJ/kg)
Coal	as rec'd	as rec'd	as rec'd	as rec'd	as rec'd
Shipment 1	1.83	10.48	41.76	45.93	29620
Shipment 2	5.48	8.68	38.62	47.5	n/a

Table 2-2. Ultimate analyses of two shipments of a Utah coal.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
Coal	DAF	DAF	DAF	DAF	DAF
Shipment 1	79.31	6.29	1.53	0.59	12.28
Shipment 2	80.60	5.99	1.56	0.62	11.2

2.3 Combustion Simulations

To assist with the analysis of the experimental data, computer simulations were utilized to predict experimental behavior in the axisymmetric U furnace as a function of combustion parameters. The computer model used for the simulations, JASPER, is a steady-state, axisymmetric, computational fluid dynamics code developed by Professor Philip Smith at the University of Utah. The code fully couples the effects of reacting gases and particles with the impacts of turbulence and radiation.

The turbulence is simulated using a two-equation model (κ - ϵ) for closure. The gas phase equations are solved using an Eulerian framework and the coal particle trajectories, solved in a Lagrangian framework, are coupled with the gas phase equations through particle source terms in

Table 2-3. Particle size distributions of two shipments of a Utah coal.

	Particle Size (μm)	Cumulative % Retained
Shipment 1	300	0.6
	125	13.2
	75	37.0
	45	78.2
	<45	100.0
Shipment 2	300	19.6
	125	65.5
	75	84.3
	45	98.5
	<45	100.0

both mass and energy continuity equations. The gas phase kinetics are assumed to be mixing limited; therefore, the gaseous combustion is modeled using a statistical probability density function based on the mixture fraction of the inlet streams. The statistics of the mixing of the coal off-gas is similarly computed. Coal devolatilization, char oxidation, and particle swelling and fragmentation are included in the comprehensive simulation based on time-mean properties of the surrounding gas phase. Particle and gas phase radiation are modeled using the discrete ordinates method.

Although the gas phase kinetics of the major species are assumed to be limited by the turbulent mixing and can therefore be described using local instantaneous equilibrium, the formation of NO_x is limited by its reaction kinetics and must be described by kinetic rates. As the impact of NO_x chemistry is small with respect to other processes affecting the turbulence and heat transfer within the combustion chamber, the computation of NO formation and destruction is delayed until after a converged flow field is obtained. Therefore, the effects of turbulent fluctuations can be fully coupled with the reaction kinetics. The rate of formation of NO due to thermal, prompt, and fuel-N mechanisms are included. The fate of fuel-N is determined by different mechanisms depending on whether the nitrogen evolves with the volatiles or is associated with the residual char.

2.4 Discussion of Results

2.4.1 NO_x Formation in a Hot-Walled Furnace

Since mechanisms of fuel-N oxidation and molecular nitrogen fixation (thermal NO_x) are strong functions of temperature, the constraint that the HITAF furnace be a hot-walled, nearly adiabatic system increases the challenge of NO_x reduction. Prior to detailed aerodynamic NO_x control experiments, the test facility was run under conventional combustion conditions to characterize NO emissions from a hot-walled furnace. The burner detailed in Figure 2-3 was run in swirl mode, i.e. incoming secondary air was heated to 535 K and passed through the swirl vanes into the quarl. The swirl number was assumed to be large because the only axial component of momentum came from the coal-carrying primary air jet. The coal firing rate was 32.2 kW. As expected for this system and burner configuration, exhaust NO emissions were approximately 920 ppm. These results can be compared to NO emissions from the gas stabilized, all axial flames described in the next section.

2.4.2 The Use of Stabilization Gas

Research funded by the U. S. Environmental Protection Agency (EPA) in the early 1970's (Heap et al., 1990) indicated that relatively low NO_x emissions could be achieved with naturally staged, axial flames, but that flame stabilization on the burner injector was critical in obtaining low NO_x emissions from an axial, pulverized coal flame. Rapid near field fuel/air mixing, achieved by injecting the fuel radially into the secondary air, stabilizes the flame and decreases flame length but greatly increases fuel-N oxidation. Axial fuel injection retards this near field mixing, resulting in a naturally staged flame with reduced NO_x emissions. If the point of flame ignition is displaced from the fuel injector tip due to an ignition delay, significant secondary air entrainment can occur prior to ignition, enhancing fuel-N oxidation. This effect of delayed ignition on NO_x formation has also been noted by Asay et al. (1983). The key to reduced NO_x levels is to retard early secondary air entrainment while maintaining the point of ignition at the injector tip.

Experiments were conducted to evaluate the possibility of using small amounts of natural gas to enhance the stabilization of very slowly mixed, axial coal flames. Presently, low-NO_x burner technologies introduce optimized swirl into the secondary air stream to stabilize the flame on the fuel injector tip (Heap and Folsom, 1990; Abbas et al., 1993). Nevertheless, the current research into the effects of using gas stabilization is needed for several reasons. First, the use of swirl for flame stabilization in the HITAF furnace could increase operational problems. The HITAF design depends upon heat transfer through a thin layer of running slag, and the use of swirl could increase slag buildup by imparting tangential momentum to the burning coal particles. Second, the use of gas to stabilize the flame may prove more effective than swirl air in reducing NO_x formation in the near burner region.

To explore the effects of gas stabilization, the fuel injector tip was located 0.74 quarl lengths downstream from the burner throat and the amount of axially injected stabilization gas was varied while the coal firing rate was held constant. Primary air was also varied to maintain a constant fuel (coal + stabilization gas) to primary air stoichiometry. Smart et al. (1988) have studied the effect of the axial location of the end of the coal injector, but their work does not include the use of stabilization gas.

The results of varying the stabilization gas on exhaust NO levels are shown in Figure 2-4. The NO level remains constant at approximately 420 ppm as the gas firing rate is

Figure 2-4. Importance of gas stabilization. Burner tip is located 0.74 quarl lengths from burner throat. Coal (shipment 1) firing rate is 25.8 kW.)

reduced to about 1.7 kW. However, when the gas is shut off, NO production immediately jumps to 830 ppm. When gas is supplied once again, NO levels do not return to 420 ppm until the gas firing rate reaches 10.2 kW. The cause of the sudden rise in NO formation when stabilization gas is shut off is delayed ignition, as described above. During the experiment, the flame visibly dropped at least a 0.3 m from the bottom edge of the quarl when stabilization gas was shut off. The flame remained visibly detached from the injector tip until the gas firing rate reached 10.2 kW. Only then did the flame front move back up into the burner quarl.

To improve flame stabilization, the fuel injector tip was moved to a location 0.12 quarl lengths downstream from the burner throat. The above experiment was then repeated, with the exception that primary air was held constant. The results are shown in Figure 2-5 (A); data taken on two different days are plotted to show the magnitude of the scatter in the data. NO exhaust emissions are again relatively flat above a gas firing rate of 3 kW. Below 3 kW, the NO profile rises gradually from 440 ppm to 600 ppm; there is no large jump like that seen when the fuel injector was located farther down the quarl throat. Hysteresis effects are very small; the flame reattaches easily as the gas level is increased from zero. Also, there was no visual indication that the flame front had dropped as in the previous experiment. The increased stability of the flame for these conditions is likely due to the fuel injector being closely surrounded by a hot refractory quarl which provides a strong radiant source. Thus, placement of the fuel injector tip appears to have removed the hysteresis effect but not the need for gas stabilization to reduce NO formation in the near burner region. Also note that only a small amount of gas (less than 10% of the total energy input) is needed to anchor the flame and minimize NO emissions from the all axial flame. Use of additional gas has little impact.

The importance of primary stream O₂ concentration in the success of stabilization gas injection is shown Figure 2-5 (A) and (B). O₂ concentration in the primary stream is 21% in Figure 2-5 (A) and 13% in Figure 2-5 (B) with primary jet velocity being held constant. A comparison of these two flame conditions reveals that general trends are similar for both cases; below a gas firing rate of 3 kW, the NO profiles rise by almost 200 ppm. The surprising result of this comparison is that NO emissions do not change as primary O₂ concentration is decreased from 21% to 13%. This observation will be addressed in the following section. Nevertheless, it is evident from the slight hysteresis effect in Figure 2-5 (B) that lowering the primary O₂ concentration has a destabilizing effect on the gas-stabilized flame and should be avoided if possible.

Finally, the stabilization gas injection scheme could influence flame stability, ignition front location, and NO production. To test this possibility, the velocity of the injected gas was altered using the removable gas stabilization insert shown in Figure 2-3. Without the insert, gas exited the fuel injector through an annular ring. With the insert, natural gas exited the fuel injector through eight discrete axial jets parallel to the primary coal jet. The total cross sectional area of the annular ring was 1.69 cm² while that for the eight holes was 0.23 cm². As in previous experiments, the stabilization gas firing rate was varied while the coal firing rate was held constant. At a gas firing rate of 3 kW, the velocity of the gas exiting through the annular ring was 5.9 m/s while that exiting through the discrete jets was 43.4 m/s.

The results of this comparison are seen in Figure 2-6. Clearly, the gas injection velocity and/or configuration has only a slight effect on NO production. At gas firing rates above 1 kW, the maximum difference in NO emissions between the two cases is 30 ppm. Of interest in Figure 2-6 is the influence of gas injection configuration on the amount of stabilization gas needed to securely anchor the flame on the fuel injector. With the lower velocity, annular ring configuration, it is possible to reduce the gas firing rate to 0.5 kW

Figure 2-5. Effect of primary air stoichiometry and gas stabilization. Burner tip is located 0.12 quarl lengths from burner throat. Coal (shipment 1) firing rate is 29.4 kW. Primary jet velocity is 17 m/s.

Figure 2-6. Comparison of stabilization gas injection schemes. Coal (shipment 2) firing rate is 28.7 kW.

while still maintaining NO levels below 360 ppm. An explanation for this effect is that the natural gas exiting through the annular ring forms a uniform shroud of rapidly igniting fuel around the coal jet while the gas exiting through the discrete jets provides only discrete coverage.

2.4.3 Primary Jet Velocity and Stoichiometry

In addition to stabilization gas effects, initial experiments indicated that the primary air flow rate had a significant impact on NO production from the all axial burner configuration. This trend is in agreement with earlier work by Heap et al. (1973, 1990) on flames with axial fuel injection and swirl but without gas stabilization. However, varying the primary air flow rate changes two important parameters: primary stoichiometry (quantity of O₂ immediately available to the coal particles) and primary jet velocity. According to the early work of Heap et al. (1975), both these factors play an important role in the conversion of fuel-N to NO_x. The data plotted in Figure 2-5 indicate that the situation might be different in the current configuration, i.e. a hot-walled combustor with a gas stabilized, naturally staged flame. As explained previously, varying the O₂ concentration from 13% to 21% in the primary stream had little effect on in-flame NO production levels.

To investigate the mechanism causing this effect, experiments were conducted such that primary stoichiometry and jet velocity could be varied independently. A metered nitrogen (N₂) stream was introduced into the primary air such that the amount of O₂ in the primary stream could be varied simply by changing the ratio of primary air to N₂. A suitable volumetric flow rate for transporting the pulverized coal was chosen and held constant while the relative quantities of primary air and N₂ were varied to yield O₂ concentrations in the range of 10%-21%. The stabilization gas firing rate was held constant at 2 kW.

The results are seen in Figure 2-7 for experiments conducted on two different days.

Figure 2-7. Influence of primary jet velocity and primary air stoichiometry. Coal (shipment 1) firing rate is 29.4 kW. Stabilization gas firing rate is 1.8 kW.

Data are plotted as a function of primary jet stoichiometry for different jet velocities. All jet velocities were calculated based on primary air at ambient conditions because of the difficulty of measuring the temperature of the primary jet as it exits the burner. The important observation from this figure is that increasing the O₂ content of the primary jet had essentially no impact on NO emissions at the levels tested. Under the conditions of these experiments, the effect of primary air flow rate on NO production was primarily due to changes in primary jet velocity. Decreasing the nominal jet velocity from 26.6 m/s to 14.0 m/s (open symbols) cut the NO emissions by a factor of two with these gas stabilized, axial flames. In all cases, secondary air velocity was approximately constant at 6-7 m/s.

Further testing at primary jet velocities greater than 30 m/s and less than 12 m/s was unsuccessful. At velocities greater than 30 m/s, ignition occurred beyond the viewing range of the flame detection safety system. At the low flow rates necessary to produce velocities less than 12 m/s, the eductor through which coal was fed became plugged up.

The result of increasing primary jet velocity is similar to that of decreasing the stabilization gas to zero. Instead of being anchored on the injector tip, the higher velocity flames are partially lifted. A lifted flame entrains O₂ from the secondary air stream prior to ignition, thus increasing local O₂ availability to the devolatilizing fuel-N. A secondary effect that would also enhance NO formation results from shear layer mixing. As the velocity difference between the primary and secondary streams increases, so does the shear layer mixing, which rapidly entrains increasing amounts of secondary air into the outer layers of the coal jet, resulting in local NO formation.

Due to the difficulties of observing flame standoff distance during the tests and in order to obtain mechanistic insight, computer simulations were performed using JASPER for a high jet velocity case (26.6 m/s) and a low jet velocity case (14.0 m/s).

CO profiles for the two simulations are compared in Figure 2-8. There are several important observations to be made. First, this comparison reveals that the high velocity flame is lifted far beyond the end of the quarl while the low velocity flame ignites at the end of the quarl. Second, the regions of highest CO concentration in the two CO profiles differ in magnitude and length. The low velocity case has higher CO concentrations over a longer distance. This concentration difference indicates that O₂ from the secondary air stream has indeed been entrained prior to ignition in the high velocity case. Since more O₂ is available, CO levels are lower and CO is more rapidly oxidized to CO₂. The O₂ profiles also support this entrainment theory. In the low velocity case, O₂ drops to zero as CO reaches its maximum and remains at zero over a range of several axial node points. In the high velocity case, O₂ drops to zero at only one axial node point, again indicating the increased availability of O₂ for this case. The predicted maximum temperature in both flames is approximately 1940 K.

To further test these results, the primary air tube in the burner was substituted for a tube of slightly larger diameter. The diameter of the original tube was 1.07 cm while that of the enlarged tube was 1.32 cm. Increasing the tube diameter changes the primary jet velocity without changing jet stoichiometry. In each case the stabilization gas was injected through eight distinct holes with a total cross sectional area of 0.23 cm². Holding both primary air flow rate and coal feed rate constant, data were collected using the original smaller diameter tube (jet velocity = 12.9 m/s) and the larger diameter tube (jet velocity = 8.4 m/s) with various stabilization gas firing rates. The NO emissions from the larger diameter tube were 75-100 ppm lower for all gas firing rates. This trend is consistent with that seen in Figure 2-7 and emphasizes the importance of primary jet velocity on NO emissions.

Figure 2-8. JASPER generated CO profiles for two cases from Figure 2-7. Low velocity = 14.0 m/s; high velocity = 26.6 m/s.

2.4.4 Vitiated Oxidant

The use of natural gas stabilization and the variation of primary jet velocity significantly affect near burner aerodynamics and, consequently, NO formation. This research has focused on near burner combustion modifications in a hot-walled furnace similar to the HITAF configuration, and one of the constraints of the HITAF system is that the combustion air is actually a vitiated oxidant containing 17.6% O₂. Therefore, it is desirable to understand the effects of using a vitiated oxidant with the naturally staged, gas stabilized burner to determine whether variations in O₂ concentration in the secondary stream also influence near burner NO formation. The vitiated oxidant was produced by heating a normal air stream to 615 K and then passing it through the hot gas generator. In the hot gas generator, the heated air was mixed with the combustion gases from a natural gas burner fired at 11.1 kW. Pure O₂ was then added to bring the resulting O₂ concentration to the desired level. The temperature of the vitiated oxidant entering the hot-walled combustor was 755 K (vs. 535 K for electrically preheated air).

Figure 2-9 presents a comparison plot of NO emissions as a function of gas firing rate for normal secondary air and for vitiated oxidant (17.5% O₂). Primary air flow rate (nominal velocity = 16.5 m/s) was held constant between the two cases. The data are reported in mg NO₂/10⁶ J (and lbs NO₂/10⁶ BTU) in order to eliminate the dilution effect of the vitiated oxidant on absolute NO levels. In reporting the data this way, the total energy input includes the stabilization gas and the pulverized coal but not the gas used to fire the burner in the hot gas generator. NO emissions for the vitiated air condition are slightly higher than those for the normal air condition at all stabilization gas firing rates; with no stabilization gas addition, NO emissions are nearly identical for both conditions. Other results suggest that the vitiated air introduces some flame instability and that the flame attachment may be less secure for a given gas flow rate.

To further understand the similarity in NO emissions for the two conditions, two cases were simulated using JASPER and the predictions are included for comparison in Figure 2-9. Although experimental and modeling results do not perfectly agree on an absolute scale, the model correctly predicts that NO emissions for both cases are nearly identical at zero gas stabilization. A look at the modeling results reveals some possible explanations for the observed experimental results. To begin with, although overall stoichiometry remains unchanged when switching from normal to vitiated air, the use of vitiated air alters the mixing in the near burner region, which affects local stoichiometries and temperatures. Local fuel/oxidant mixing is influenced by the increase in secondary jet velocity and by the reduced O₂ availability that result from the vitiation process. As a result, the predicted point of ignition for the normal air case is located one quarl length down the furnace while that for the vitiated air case is 1.5 quarl lengths down the furnace. As noted earlier, a lifted flame leads to entrainment of the secondary air stream. Thus, even though O₂ concentration in the vitiated air case is only 17.6%, O₂ availability at the point of ignition is enhanced by increased entrainment of the secondary stream. Any benefit of reduced NO formation due to the reduced O₂ concentration in the vitiated air appears to be nullified by this vitiated air entrainment in the lifted flame.

Figure 2-9. Comparison of normal air versus vitiated oxidant. Coal (shipment 1) firing rate is 29.4 kW with normal air and 25.8 kW with vitiated air. Primary jet velocity is 17 m/s.

Next, the predicted post-ignition combustor temperature profiles are similar for both cases although post-ignition temperatures for the normal air case are consistently slightly higher. The highest predicted temperature in the normal air case is 2065 K while that in the vitiated air case is 150 K lower. Prior to ignition, the vitiated air case is 220 K hotter than the normal air case. These higher temperatures in the preflame zone enhance early NO formation (vitiated air case) while higher temperatures in the flame itself also promote NO formation (normal air case).

All these competing effects appear to compensate each other and are secondary to the issues of stabilization gas firing rate and primary jet velocity on NO formation in a hot-walled system with a naturally staged burner. In general, the NO emissions were also very similar for other experimental comparisons of the two cases, including variation of the primary air velocity and staged combustion.

2.4.5 Ultra Low NO Levels Using Near Burner Optimization with Air Staging and Gas Reburning

The ability to achieve ultra low NO levels results from optimizing each furnace region for NO reduction and N₂ formation. This paper has explored the important parameters in the near burner region using a naturally staged, gas stabilized burner. Despite the challenge of a hot-walled combustor, NO levels below 350 ppm have routinely been achieved with this burner using optimized gas stabilization and primary jet velocity (see Figure 2-6 and Figure 2-7). The final step in this study was to determine the lowest levels of NO that could be obtained from the optimized use of an all axial, gas stabilized, pulverized coal flame in conjunction with the proven in situ NO_x reduction techniques of air staging and natural gas reburning.

Figure 2-10 shows results from operating the axial flame in staged combustion mode. Data are plotted as a function of stage one stoichiometry for two different first stage residence times. At the longer residence time (990 ms), NO levels near 175 ppm are achieved if the first stage is operated at a stoichiometric ratio of approximately 0.85. Even lower NO emissions can be achieved if staged combustion is followed by gas reburning.

Figure 2-11 shows experimental results for two different primary jet velocities under optimized staged combustion conditions with gas reburning. Data are plotted as a function of overall stoichiometry in the reburn zone. Stabilization gas was held constant at 2.0 kW. The primary zone stoichiometric ratio was 0.75, followed by staged air addition at 990 ms to raise the overall stoichiometric ratio to 1.05. Varying amounts of reburn gas were added through ports at 1190 ms, and enough burnout air was injected through ports at 1720 ms to bring the overall stoichiometric ratio at the exit of the combustion chamber to 1.15. NO emissions below 90 ppm were attained without any downstream SCR or SNCR. An understanding of the effect of near burner aerodynamics on NO production was critical to achieving these ultra low levels in a hot-walled furnace.

Figure 2-10. Effect of air staging for two different stage one residence times. Co: (shipment 1) firing rate is 29.4 kW. Stabilization gas firing rate is 1.8 kW. Primary jet velocity is 17 m/s.

Figure 2-11. Ultra low NO emissions using optimized burner modifications in conjunction with air staging and gas reburning. Coal (shipment 1) firing rate is 29.4 kW, stage two stoichiometry is 1.0, and final burnout stoichiometry is 1.15.

3.0 Experimental Studies on Char N Oxidation

One of the main goals of this project is to provide new information about the role of char-N in NO_x formation in pulverized coal combustion. Because this goal is broad in scope, five objectives helped narrow and define the scope of the project. These five objectives are:

1. Isolate char-N from volatile-N in order to study char-N.
2. Collect all data at pulverized coal conditions so that results are relevant to what actually occurs in pulverized coal combustors.
3. Determine the effect of various combustion parameters (i.e., O₂, furnace temperature, local NO_x concentration, parent coal, etc.) on the formation of NO_x from char-N.
4. Obtain a reliable data set for use in char-N model development/validation.
5. Identify current char-N models which may explain the observed experimental results and/or outline modifications which could be made to existing models to explain experimental data.

Experimental studies addressing the first four objectives are discussed in this section with a char-N modeling discussion giving in the following section. Although some experimental detail is given in this section, more information may be found in the appendices of this report.

3.1 Experimental Design

3.1.1 Burning a Simulated Coal

To begin, NO_x formation from char-N is most easily studied by first removing all the volatile-N. Volatile-N can be removed by devolatilizing the parent coal and collecting the resulting char. In lower rank coals, char oxidation rates are fast enough to compete for O₂ with the volatile portion of the coal (Niksa and Cho, 1996), so chars collected from lower rank coals may exhibit significant carbon burnout. This char can then be burned to obtain data on char-N conversion to NO_x. However, if the char is burned without any additional fuel source, the char flame will be difficult to ignite and sustain, and the conditions under which the char burns will not be representative of what happens in a pulverized coal flame, where volatiles combustion increases the local flame temperature and radiant heat flux to the char particles and decreases the local O₂ concentration. The solution to this dilemma is to burn a simulated coal. This simulated coal should have a nitrogen-free volatile component, a nitrogen-containing coal char component, and an optional volatile-N source that can be varied independently of char-N and from which NO_x levels can be quantified. A diagram of the simulated coal chosen for these experiments is shown in Figure 3-1. Natural gas is a reactive, nitrogen-free fuel which replaces the coal volatiles. It is burned

Figure 3-1. Schematic drawing of simulated coal and real coal.

simultaneously with the coal chars to be studied. A quantifiable source of nitrogen which simulates volatile-N is produced by doping the flame with either NH₃ or NO.

Burning a simulated coal solves the problem of isolating char-N from volatile-N. Nevertheless, a major dilemma still exists regarding char production. Under what conditions should the chars be produced? Factors such as peak temperature, residence time, heating rate, and gas environment affect the physical and chemical structure of the char. Hyde et al. (1989) found that coal char reactivity varied greatly depending on coal rank and preparation method. Other researchers (Hecker et al., 1992; Solomon et al., 1992; Smith, 1982) have also reported the effects of devolatilization conditions on coal char reactivity. White et al. (1991) compared N₂ BET surface areas reported for chars prepared by different methods from Pittsburgh #8 coal and found a wide disparity. They concluded that “chars should be prepared either in a flame or in the presence of O₂ in order for their properties to be characteristic of char evolved in combustion.”

Ideally, the coal chars used in these experiments would be representative of coal chars found in the latter stages of pulverized coal (pc) flames. Thus, these coal chars would need to be prepared with heating rates (10⁴-10⁵ K/s), peak temperatures (1700-2000 K), and gas

environments similar to those found in pc flames. Researchers studying char reactivities and char oxidation rates have found char production methods that meet these requirements including entrained flow reactors and flat flame burners. In both of these configurations, fuel (methane, hydrogen, etc.) and oxidizer (N₂/O₂, Ar/O₂, air, etc.) are fed to a burner and ignited. Coal particles are then fed into the flame front and char is collected at various distances from the flame front (Mitchell et al., 1992; Reade and Hecker, 1994; Field, 1970; Hurt, 1993). Gas temperatures commonly reported are in the 1700-2000 K range. Leslie et al. (1989) used an alternate argon arc-jet technique to get gas temperatures between 1000-2000 K. In all cases, heating rates are typical of pc conditions.

Researchers looking at char-N issues have taken a variety of approaches to char production. Thomas et al. (1993) used carbon-13 doped with nitrogen, de Soete (1990) devolatilized coal under argon flow at 1450 K, and Ninomiya et al. (1989) pyrolyzed coal in an oxygen-free atmosphere at various temperatures. However, none of these methods meets the requirements of heating rate, peak temperature, and gas environment for char production at typical pc conditions. Experimental conditions similar to those in pc flames were successfully reproduced in an electrically heated resistance furnace by researchers at MIT. Chars were produced under pyrolytic conditions (Pohl and Sarofim, 1973; Song et al., 1982a) and subsequent data relating to the fate of char-N were obtained.

The present experiments put an additional requirement on char production because of the size of the combustor used for the study, a 29 kW U-shaped furnace described in detail in “Design of the U Furnace” on page 123. The char production methods which best simulate pc conditions (entrained flow reactor, flat flame burner) were not designed to produce chars for a 29 kW combustor. Fortunately, the combustor itself can be used for char production if several precautions are taken. First, the burner must produce a well-mixed coal/air flame so that all coal particles see a similar gas environment as they move through the furnace. Only a well-mixed flame will assure that char particles are formed as uniformly as possible. This type of flame can be achieved with a premixed burner. The premixed burner which was designed and built for the present experiments is described in “Premixed Burner Design” on page 136. Second, conditions in the combustor must simulate those in a typical pc flame. Measured peak temperatures in the U furnace are in the range of 1700-2000 K when firing with pulverized coal. These peak temperatures and the presence of a self-sustaining coal flame indicate that pc conditions exist.

Once the char is produced, it must be collected. Details of how and under what conditions the chars used in this study were produced and collected are given in the appendices.

3.1.2 Experimental Protocols for Simulated Coal

Once the coal chars have been produced and collected, several protocol issues need to be addressed. First, at what relative firing rates should the natural gas and char be represented in the simulated coal? One possibility is to compute carbon loss between the parent coal and the char and then “replace” that carbon with an equivalent amount of

carbon in the form of natural gas. However, matching carbon loss is not necessarily the best method because the carbon to hydrogen ratio is much higher in natural gas than in coal and heating values are different for the two fuels. A second possibility is to perform experiments at various natural gas and char firing rates to determine the most reasonable firing rate for each fuel based on the effects of relative firing rates. Such experiments would require large quantities of time and char supplies, neither of which were available. A third possibility is to use the same natural gas and char firing rates in all experiments. Such firing rates could be roughly based on the “replacement” concept described above.

For most of the experiments in this study, natural gas and char firing rates were held constant at 24.9 kW and 4.4 kW respectively. These firing rates were roughly based on the “replacement” concept as most chars were collected in the latter stages of burnout (degree of char burnout ranged from 69-87%).

A second issue relates to doping the flame with NH₃ or NO. In preliminary tests, doping was accomplished by adding NH₃ to the primary air stream that carried the char into the burner. This doping method was dropped in favor of adding NH₃ or NO to the natural gas stream just prior to its entering the burner. Doping the natural gas achieves the desired effect because the simulated coal volatiles (the natural gas) are mixed with the simulated volatile-N (NH₃ or NO) before entering the burner.

A third issue to consider is thermal NO_x formation in coal and gas flames. Thermal NO_x results from the oxidation of atmospheric nitrogen in high temperature flames. Included in the char-N experimental matrix were tests which required the elimination of thermal NO_x formation such that the only source of nitrogen in the system was char-N. For these tests, a nitrogen-free oxidant would have to be used instead of air. An oxidant mixture consisting of Ar, CO₂ and O₂ was selected because it is nitrogen-free and the gases are relatively inexpensive to obtain in large quantities. Also, the ratio of Ar to CO₂ in the mixture can be varied such that adiabatic flame temperatures for the oxidant + fuel vary over a range of several hundred Kelvin.

3.1.3 Parameters Tested with the Simulated Coal

Many factors affect char reactivity and rates of char oxidation and, by extension, char-N reactivity and oxidation. Coal rank has been implicated by many researchers as a primary factor in char reactivity (Field, 1970; Hyde et al., 1989; Smith, 1982). Also, because char reactivities are kinetic expressions, they are strong functions of temperature (Smith, 1978). Finally, since consumption of char in a pc flame is thought to occur mainly through oxidation (Smoot, 1993), O₂ concentration in the combustion system strongly influences char oxidation. Hence, coal rank, flame temperature, and O₂ concentration were chosen as three of the parameters to be tested during the char-N experiments.

How was each of these parameters tested? Coal rank was studied by using five different coals in the experiments: three bituminous, one subbituminous, and one lignite. Flame temperature was varied two ways. One, the electric heaters used to preheat the

combustion air, normally on, were turned off. Adiabatic flame temperatures with the heaters off are at least 100 K lower than with the heaters on. Two, as mentioned previously, adiabatic flame temperatures with Ar/CO₂/O₂ as the oxidant can be varied by changing the relative amounts of Ar and CO₂ in the oxidant mixture. Mixtures containing 0%, 15%, and 25% CO₂ were used; natural gas adiabatic flame temperatures vary by approximately 500 K for this range of CO₂ concentrations. Lastly, O₂ concentration was varied by increasing the amount of available oxidant (either air or Ar/CO₂/O₂).

In addition, two parameters unique to char-N reactions were selected for subsequent testing in the char-N experiments. First was the weight percent nitrogen in the char. Does a low-nitrogen char produce different results than a high-nitrogen char? Since most proposed char-N kinetic mechanisms require the char carbon to nitrogen ratio as an input, it is likely that weight percent nitrogen in the char is a key factor. Varying the weight percent nitrogen in the char was accomplished by choosing parent coals with widely varying nitrogen contents (0.85-1.76% on a dry basis). Also, a commercial char with high carbon content and extremely low nitrogen content (0.13% on a dry basis) was added to the test matrix.

The second char-N specific parameter selected for study was the concentration of NO_x in the gas phase. One char-N kinetic mechanism proposes that gas phase NO in the pores of a particle reacts with bound nitrogen in the char to form N₂O (Goel et al., 1994). Other mechanisms include the reduction of gas phase NO_x on the surface of the char as an important reaction (Shimizu et al., 1992; Peck et al., 1991). Varying levels of NO_x in the gas phase were achieved by adjusting the flow rates of the doping gases (NH₃ or NO) into the natural gas stream.

Finally, two parameters related to the design of the experiments were added to the test matrix. These parameters are the firing rates of char and natural gas, chosen to be 24.9 kW and 4.4 kW respectively for reasons discussed in “Experimental Protocols for Simulated Coal” on page 26. However, some question remains regarding the effect of firing rate. If the char firing rate is increased while the natural gas firing rate is held constant, char loading is increased, which has implications for NO_x reduction on the char surface and for NO_x production from the char. Thus, in a few experiments the natural gas and char firing rates were varied, although lack of time and char supplies limited the testing.

3.1.4 Data Collection with the Simulated Coal

The data collected during any experiment should reflect the type of information that is desired from the experiment. In the present experiments, both solid and gas phases were present. The data collected reflect both the presence of two phases and the types of parameters being studied. Solid phase data were obtained by subjecting the various chars and their parent coals to a variety of tests including proximate and ultimate analyses, N₂ BET surface area and porosity, and SEM photos of the external particle structures. Details of these measurements are found in “Characterization of Chars” on page 190. Gas phase data were obtained using sample probes inserted into the furnace during the experiments.

Gas phase concentrations of O₂, CO₂, CO, and NO_x species (NO₂, NO, N₂O) were measured using the analytical instruments described in “Instrumentation/Data Collection” on page 153. Furnace temperatures were also measured and recorded; see “Temperature Measurement in the U Furnace” on page 174.

3.1.5 Experiments with the Parent Coals

As part of the experimental matrix, the parent coals of all the coal chars except Black Thunder were tested. These coal experiments were included for two reasons: one, to study how various furnace operating parameters influence the simulated coal vs. the parent coal and two, to gain additional insight into the char-N results based on comparisons of simulated coal to parent coal data.

The firing rate was held constant at 29.3 kW while the effects of coal type, O₂ concentration, and furnace temperature on NO_x emissions were tested. Each coal was also burned in Ar/CO₂/O₂ to eliminate thermal NO_x contributions to the measured NO_x. Gas phase data from the parent coal experiments were obtained by the methods described above for the simulated coal.

3.2 Fate of Char-N: Artificial Oxidant Results

After confirming the consistency of the baseline data and the effects of the chosen operating conditions, a presentation and an analysis of the char-N experimental data can begin. The experiments described in this section were all conducted in artificial oxidant, thus eliminating any effects of NO_x sources other than the char-N itself. Unless otherwise indicated, the overall stoichiometric ratio was 1.15.

3.2.1 Influence of Parent Coal Composition

The first parameter to be considered is the effect of parent coal type on the conversion of char-N to NO_x when firing simulated coals in artificial oxidant (Ar/15%CO₂/O₂). Data from five different parent coals are plotted in Figure 3-2. Within each parent coal grouping are data from all the chars collected from that parent coal; some bars represent repeat tests with the same char. The char-N to NO_x conversion levels for each parent coal grouping are clustered together. In general, the char-N to NO_x conversions of the lower rank coal chars (Knife River and Black Thunder) is higher than those of the three bituminous coals. The lower rank coal chars have much lower carbon and nitrogen contents than the bituminous coal chars, which may affect the availability of reactants for mechanisms which lead to N₂, not NO_x production.

The conversions of char-N to NO_x in Figure 3-2, ranging from approximately 40% to 60%, are high. A comparison of these results to those obtained by other researchers burning coal chars in artificial oxidant reveals both similarities and differences. Early work by Pershing and Wendt (1979) burning a coal char with small amounts of methane in a

Figure 3-2. Data for char-N to NO_x conversions in Ar/15%CO₂/O₂ grouped by parent coal type of the chars.

laboratory scale furnace yielded char-N to NO_x conversions of less than 20%. 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. (1982b) also reported char-N to NO conversions of less than 20% when burning a coal char with propane in an artificial oxidant of Ar/25% O₂. No details were given about the preparation of the char.

Other researchers have reported results in the same range as those shown in Figure 3-2. De Soete (1990) reported fractional conversions of char-N to NO of 0.35 to 0.67 for highly devolatilized bituminous coal chars burned in an Ar/O₂ mixture in a fixed bed reactor. Shimizu et al. (1992) pyrolyzed nine coals in a fluidized bed pyrolyzer and then measured the fractional char-N to NO_x conversions of the chars burned in an Ar/3.15% O₂ mixture in a fixed bed reactor. They measured conversions between 0.2 and 0.5. A third group of researchers (Song et al., 1982b) oxidized lignite chars prepared at 1250 K and 1750 K in an electrically-heated furnace at two different temperatures, 1250 K and 1750 K. The oxidant was a He/O₂ mixture. At 1250 K, the conversion efficiency of char-N to NO_x was 44% while at 1750 K, the conversion efficiency dropped to 30%.

In recent work by Wang et al. (1996), chars were prepared from two bituminous coals (high-volatile and low-volatile) by subjecting the coals to various heating rates and final

temperatures in a wire mesh reactor. The chars were subsequently burned in an Ar/20% O₂ mixture. Chars prepared from the high-volatile bituminous coal at final temperatures up to 1473 K yielded fractional conversions of char-N to NO from 0.11 to 0.15; fractional conversions for chars prepared from the low-volatile bituminous coal at final temperatures of 1273 K were 0.25 and 0.32. Not only are these conversions, especially for the high-volatile bituminous coal, much lower than the conversions in Figure 3-2, the trend with coal rank is reversed. However, Wang et al. did prepare one char from the high-volatile bituminous coal by heating the coal to 1773 K, a temperature more representative of pc conditions, and the fractional conversion of char-N to NO for that char was 0.49.

It is difficult to directly compare the results from all these researchers to the current work because of the range of conditions under which the coal chars were prepared and oxidized. Also, mixtures containing Ar gas were used by many of the researchers while NO_x species were measured with a chemiluminescent NO_x analyzer. It is now known that Ar suppresses the chemiluminescent signal (see discussion beginning on page 161). Nevertheless, comparisons of the present data set to the work of other researchers emphasizes the importance of the present work. It is the only data set currently available in which the chars were prepared at pc conditions, the char-N experiments were conducted at pc conditions, and all NO_x measurements were made using two different instruments.

The char-N to NO_x conversion data shown in Figure 3-2 are replotted in Figure 3-3 versus weight percent nitrogen in the char (dry basis). Nitrogen content on a dry basis was selected over nitrogen content on a dry, ash-free basis because of the heterogeneous nature of nitrogen removal from the char matrix. Gases which may potentially react with the char-N must first diffuse into the pores of the char, and the amount of ash present will affect how readily those diffusing gases find char-N sites. In Figure 3-3, weight percent nitrogen in the char does not correlate the data very well. Nevertheless, the differences between the grouping of lower rank coal chars around 0.5% and the grouping of bituminous coal chars between 1.0-1.6% are distinct. In comparison, Wang et al. (1994a, 1994b) 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.

A comparison of Figure 3-2 and Figure 3-3 indicates that char-N to NO_x conversion levels in artificial oxidant are more dependent on parent coal type than on nitrogen content of the char. This observation is most evident with the set of Illinois #6 coal chars, which range in nitrogen content from 1.13% to 1.61% (dry basis) but vary in char-N to NO_x conversion by only 6%. Subsequent results from tests with the Illinois #6 coal chars indicate that, under some circumstances, nitrogen content helps to correlate and explain the data.

The measured NO_x emissions from which the char-N to NO_x conversions were computed are plotted versus weight percent nitrogen in the char (dry) in Figure 3-4. These NO_x emissions have been corrected for the NO_x which results from the oxidation of the nitrogen present in the natural gas (see page 198). The measured NO_x emissions, in general, increase with increasing nitrogen content of the char. Thus, although the highest

conversion levels of char-N to NO_x in Figure 3-3 are associated with the Knife River chars, these chars have the lowest NO_x emissions because their nitrogen content is so low. Also, the char with the highest nitrogen content, Ill (18 sept), does not have the highest conversion of char-N to NO_x, but it produces the highest NO_x emissions.

Figure 3-3. Conversion of char-N to NO_x when burning simulated coals in artificial oxidant as a function of nitrogen content of the char.

In Figure 3-5, char-N to NO_x the conversion data in artificial oxidant are plotted versus N₂ BET surface area for the chars whose surface area was measured. There appears to be no correlation between N₂ BET surface area, which characterizes the mesopore and some of the micropore structure of the char (pores with radii in the range of 1.5-50 nm), and conversion of char-N to NO_x. The surface areas of the lowest and highest surface area chars differ by almost a factor of 5, but their conversions differ by only 8%. Much larger differences in conversion exist for chars with very similar surface areas.

It has been postulated by Goel et al. (1996) that most of the heterogeneous reactions occurring within the char particle occur in the mesopores with micropores being too small and macropores not having a high enough surface area to volume ratio for heterogeneous reactions to occur. Hence, one might expect that mesopore structure would have a significant effect on the fate of char-N. However, while pore structure and internal surface area may play important roles in the diffusion and reaction processes that characterize char-N conversion to NO_x, other factors in these experiments need to be considered. One conclusion that can be drawn from all these figures is that char-N to NO_x conversion is a complex issue that is not controlled by a single parameter.

Figure 3-4. Absolute NO_x emission levels measured when burning simulated coals in artificial oxidant.

Some of the data plotted in Figure 3-2 are replotted in Figure 3-6 and Figure 3-7 by parent coal type so that the repeatability of the data can be observed. Each data point is labeled with its corresponding sample name. Data for Pittsburgh #8 and Utah coal chars are found in Figure 3-6. Both Pitt (25,26,29 sept) char and Utah (13 sept) char exhibit good repeatability with replicate experiments done on different days. Figure 3-7 contains Knife River and Black Thunder char data. Replicate experiments were performed with the K.R. (31 oct, 1 nov) char on different days, and again the results indicate good repeatability.

3.2.2 Impact of Overall Excess Air

The second parameter to be considered is the effect of excess O₂ levels on the conversion of char-N to NO_x with Ar/15%CO₂/O₂ as the oxidant. The use of artificial oxidant eliminates any thermal NO_x effects since thermal NO_x is also affected by the amount of excess O₂. Two chars, Pitt (25,26,29 sept) and Ill (16 oct) were tested over a range of excess O₂ concentrations from 2% to 8%. The results are plotted in Figure 3-8 as char-N to NO_x conversion versus percent excess O₂ (dry basis) measured in the exhaust. Because these data were difficult and expensive to obtain, no data points were repeated. There is a slight but distinct increase in conversion with increasing excess O₂ levels for both Pitt (25,26,29 sept) char and Ill (16 oct) char, although there are not enough data to determine what is scatter and what is the true shape of the curve. The data in Figure 3-8

Figure 3-5. Conversion of char-N to NO_x when burning simulated coals in artificial oxidant as a function of char N₂ BET surface area.

support the mechanistic concept that increased O₂ enhances the rate of char-N or HCN oxidation to NO_x.

3.2.3 Importance of Local Flame Temperature

The third parameter to be considered is the effect of local flame temperatures on the conversion of char-N to NO_x in artificial oxidant. Local flame temperature was varied in two ways. First, the amount of CO₂ in the artificial oxidant mixture was varied from 25% to 0%; O₂ concentration was held constant at 21% and Ar made up the balance. Simulated coal adiabatic flame temperatures for this range of CO₂ concentrations were approximately 2060 K to 2560 K. Data from two chars, Pitt (19,24 oct) and Ill (14,19,20,21 sept), are graphed in Figure 3-9 as char-N conversion to NO_x versus the computed adiabatic flame temperature. While conversion decreases with increasing adiabatic flame temperature for both chars, the decrease is much more pronounced with the Ill (14,19,20,21 sept) char than it is with the Pitt (19,24 oct) char. A strong flame temperature dependence would indicate a reaction rate-controlled process; a lack of flame temperature dependence suggests a diffusion-controlled process.

What are the differences between the two chars that might explain why the Ill (14,19,20,21 sept) char exhibits a stronger flame temperature dependence than the Pitt (19,24 oct) char? The two chars are very similar in composition as noted in Table B.4 on page 192. It is possible that the physical structure of the two chars is different.

Figure 3-6. Char-N to NO_x conversion levels in artificial oxidant for Pittsburgh #8 and Utah coal chars. Chars are identified by name.

Unfortunately, no surface area or porosity data are available for the Pitt (19,24 oct) char, so such a comparison cannot be made. The finer particle size distribution of the Pitt (19,24 oct) char than that of the Ill (14,19,20,21 sept) char (see Appendix C) would tend to favor a reaction rate-controlled (i.e., temperature-dependent) process, but just the opposite is indicated by the data in Figure 3-9.

The very small dependency of char-N to NO_x conversion on temperature for the Pitt (19,24 oct) char was checked by varying the local flame temperature a second way: turning off the electric heaters which were used to preheat the secondary combustion air or artificial oxidant. The results obtained with the heaters off are compared to those obtained with the heaters on for two different mixtures of artificial oxidant in Figure 3-10. Calculated adiabatic flame temperatures with the heaters off are approximately 100 K lower than with the heaters on. Based on the data in Figure 3-9 and Figure 3-10, the effect of local flame temperature on the conversion of char-N to NO_x in artificial oxidant for Pitt (19,24 oct) char is negligible. Further discussion of other temperature-related plots is found in Section 3.3.3, Influence of Flame Temperature at Various Initial NO_x Concentrations on page 49.

3.3 Fate of Char-N: Results from Parametric Studies

The char-N results in the previous section indicate that the conversion of char-N to NO_x is a complex process of coupled physical and chemical phenomena. Results from more extensive

Figure 3-7. Char-N to NO_x conversion levels in artificial oxidant for Knife River and Black Thunder coal chars. Chars are identified by name.

testing of the chars are presented in this section. Interpretation of the results and implications of the results for modeling char-N to NO_x conversion are found in Section 4.0. Unless otherwise indicated, the simulated coal firing rates are 24.9 kW for the natural gas and 4.4 kW for the char, the overall stoichiometric ratio is 1.15, the oxidant is air, and the electric heaters for heating the secondary combustion air are on at a setpoint of 590 K.

3.3.1 Importance of Heterogeneous NO_x Reduction on Char

Many researchers have published data relating to NO reduction on char and have computed kinetic rates for the reduction reaction (Chan et al., 1983; Levy et al., 1981; Song et al., 1981a; de Soete, 1990; Furusawa et al., 1980; Teng et al., 1992; Suuberg et al., 1990; Rodriguez-Mirasol et al., 1994). All of these researchers conducted their experiments in the absence of O₂; they fed mixtures of Ar/NO or He/NO over a bed of char and computed kinetic rates for the reduction reaction based on measurements of gas concentrations in the effluent. This reduction of NO on the char surface has been proposed as a possible mechanistic explanation for the fact that char-N to NO_x conversion is not 100%.

Since the present study is concerned with the conversion of char-N to NO_x in an oxidizing environment, it was necessary to test the importance of NO_x reduction on char in such an environment. A commercially obtained activated carbon, Nuchar, was used for the experiment. The ultimate analysis of Nuchar is found in Table B.4 on page 192. It is a high carbon (86.48%, dry basis), low ash, coconut-shell based char with extremely low nitrogen

Figure 3-8. Influence of excess O₂ on char-N to NO_x conversion in artificial oxidant.

content (0.13%, dry basis). It was burned as a simulated coal like all the coal-based chars. To test the importance of NO_x reduction on char, the Nuchar-derived simulated coal flame was doped with various amounts of NH₃ and NO, and NO_x concentrations were measured before and after the addition of the Nuchar. The results of this test are plotted in Figure 3-11. The “Initial NO_x” label on the x-axis refers to the concentration of NO_x measured in the exhaust (port 6-4) when firing natural gas with enough combustion air to oxidize both the natural gas and the char (the CFR method). The y-axis was computed using the following formula

$$NO_{x, reduced} = \frac{(NO_{x, CFR} + NO_{x, Nuchar} - NO_{x, gas + Nuchar})}{(NO_{x, CFR})} \quad (1)$$

where

$NO_{x, reduced}$ = Computed reduction of NO_x by the Nuchar

$NO_{x, CFR}$ = Exhaust NO_x concentration measured by the CFR method, hereafter referred to as initial NO_x

$NO_{x, Nuchar}$ = Exhaust NO_x concentration measured when firing Nuchar-derived simulated coal in artificial oxidant. This number represents the amount of nitrogen in the Nuchar that

Figure 3-9. Influence of local flame temperature on char-N conversion to NO_x in artificial oxidant.

is converted to NO_x. Based on the artificial oxidant results, this number is 36 ppm, which means 100% of the nitrogen in the Nuchar is converted to NO_x.

$\text{NO}_{x, \text{ gas+Nuchar}} = \text{Exhaust NO}_x \text{ concentration measured when cofiring Nuchar and natural gas, i.e., the simulated coal.}$

Reduction of NO_x on the surface of the Nuchar is on the order of 10% for all concentrations of initial gas phase NO_x tested. This number is surprisingly low for several reasons. First, in the coal char artificial oxidant results shown in Figure 3-2, char-N to NO_x conversions were only 40-60%, which means 40-60% of the char-N was reduced to N₂. If only 10% was reduced on the char surface, how was the other 30-50% reduced? Second, the N₂ BET surface area of the Nuchar is at least 10 times greater than that of the coal chars. Since heterogeneous reactions are greatly affected by available surface area, Nuchar should have greater capacity to reduce NO_x than do the coal chars, but this is not the case.

Another observation from Figure 3-11 is that the percent reduction is not a function of the initial gas phase NO_x concentration, indicating a first order dependence of the reaction

Figure 3-10. Effect of turning the secondary combustion air heaters on or off on the char-N to NO_x conversion of Pitt (19,24 oct) char in two different artificial oxidant mixtures.

rate on NO_x concentration. These results are different from those obtained with the coal chars as will be seen in the next section.

Several important differences exist between this Nuchar data and the coal char data taken in artificial oxidant. One, the source of NO_x is mainly external with the Nuchar. With the coal chars burned in artificial oxidant, the source of NO_x could be internal or external, depending on whether the homogeneous HCN mechanism or the char-N oxidation mechanism predominates. Perhaps there is a greater opportunity for internally-formed NO_x that is diffusing out of the particle to be reduced to N₂ than there is for externally-formed NO_x to diffuse into the particle and be reduced. Two, both the nitrogen and ash content of the Nuchar are very low compared to the coal chars. For example, the coal chars contain five to twenty times as much nitrogen as the Nuchar. If ash and/or char-N are involved in the NO_x reduction reactions on char, the lack of low levels of NO_x reduction on the Nuchar could be explained. Three, it is possible that the chemical structures of the Nuchar and the coal chars differ greatly, although no chemical structure data are available for comparison.

Finally, as mentioned above, Nuchar has a much higher surface area than the coal chars. Using the Nuchar manufacturer's data for total pore volume (2.3 cm³/g) and N₂ BET surface area (1600 m²/g), the mean pore radius was computed based on a formula from Wheeler's parallel-pore model (Smith, 1981). The formula is

Figure 3-11. Reduction of NO_x by Nuchar as a function of initial gas phase NO_x concentration.

$$\bar{a} = \frac{2 \times V_g}{S_g} \quad (2)$$

where

$\bar{a}$ = Mean pore radius (m)

V_g = Pore volume (m³/g)

S_g = Surface area (m²/g).

The mean pore radius computed for Nuchar is approximately 3 nm, which is in the micropore range. In comparison, the computed mean pore radius for a typical coal char, based on a total pore volume of 1.0 cm³/g (White et al., 1991) and a N₂ BET surface area of 60 m²/g, is 33 nm, which is at the high end of the mesopore range.

The fact that the computed Nuchar mean pore radius is in the micropore range could indicate that much of the available Nuchar surface area is tied up in inaccessible micropores. If that is the case, NO_x reduction on the Nuchar is low because there is limited

surface area for heterogeneous reaction despite the high overall surface area of the Nuchar. Complicating the analysis, however, is the probability that as the Nuchar burns, most of the micropores are opened up and become accessible to diffusing gases. Additionally, the driving force for NO_x in the Nuchar case is into the particle, which should favor increased reduction of NO_x on the Nuchar. As for possible differences in chemical structure between the Nuchar and the coal chars influencing the results, much of the work related to the reduction of NO on char has been done with synthetically produced carbons and activated carbons. In fact, the earliest researchers to publish results of the reaction of NO with char used ashless sugar charcoal (Smith et al., 1959).

Thus, one could conclude from the data that under the conditions of these experiments, the reduction of NO_x on the surface of char is not a significant reaction.

3.3.2 Effect of Initial Gas Phase NO_x Concentration

The Nuchar experiment described above was repeated with all the coal chars. The results, shown in Figure 3-12, are reported in a slightly different manner than the Nuchar data. In Figure 3-11 (the Nuchar data), the y-axis values were determined by equation (1); in Figure 3-12, the y-axis values, "Apparent % Conversion of Char-N to NO_x", were determined using the method described in Section C.2 on page 198. The data points at 0 ppm initial NO_x were obtained by burning the simulated coal in artificial oxidant. The data points 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 NH₃.

The striking observation from Figure 3-12 is that the apparent conversion of char-N to NO_x appears to be a strong function of the initial NO_x concentration; as the initial NO_x concentration rises, the apparent conversion of char-N to NO_x decreases dramatically. In other words, with increasing initial NO_x concentration, increasing amounts of NO_x (or other nitrogen compounds which could be oxidized to form NO_x) are reduced to N₂. This result is in direct contrast to the Nuchar results, where NO_x reduction on char remained fairly constant with increasing initial NO_x concentration. Why are these two graphs dissimilar? The answer may lie in the differences between the Nuchar and the coal chars described in the previous section. Which of those differences contribute to this observed effect, and how do those differences contribute to mechanistic insights regarding the conversion of char-N to NO_x? These questions will be explored in this and the following section.

Another observation from Figure 3-12 is that the variation of apparent conversion with initial NO_x appears to be as great within a group of coal chars from the same parent coal as it is between chars from different parent coals.

In order to examine the effect of initial NO_x concentration more carefully, the data in Figure 3-12 were separated by parent coal type and plotted in Figure 3-13 through Figure 3-15. All data from initial NO_x experiments with Illinois #6 coal chars are plotted in Figure

Figure 3-12. Effect of initial gas phase NO_x concentration on the apparent conversion of char-N to NO_x for all coal chars tested.

3-13. Data were taken in air and in artificial oxidant. All points at 0 ppm initial NO_x and all data labeled "Ill (18 sept)-Ar/15%CO₂/O₂" were taken in Ar/CO₂/O₂; all other data were taken in air. The artificial oxidant data at initial NO_x levels other than 0 ppm required doping with NH₃ or NO as did all air data at initial NO_x levels greater than 150 ppm. Note that the legend includes the nitrogen content of the chars on a dry basis.

Figure 3-13. Influence of initial NO_x concentration and nitrogen content of the char on char-N conversion to NO_x for Illinois #6 coal chars. Both air and artificial oxidant data are shown.

There are two obvious trends in Figure 3-13. The first, as noted previously, is that apparent conversion of char-N to NO_x is a strong function of initial NO_x concentration. The second is that as the nitrogen content of the char (dry basis) increases, the apparent

conversion of char-N to NO_x also increases at all initial NO_x levels except 0 ppm. In fact, as the initial NO_x concentration increases, the difference in conversion between chars of varying nitrogen content becomes more pronounced with the largest differences occurring at the highest initial NO_x level (850-900 ppm).

In light of these results, is interesting to consider the N₂ BET surface areas of the Illinois #6 coal chars, of which three were measured. The Ill (18 sept) char had the highest measured surface area of any char at 104.8 m²/g. The Ill (16 oct) char and the Ill (14,19,20,21 sept) char had identical nitrogen contents, but their measured surface areas were 71.5 m²/g and 57.6 m²/g respectively. One might expect the char with the largest surface area for heterogeneous reduction, Ill (18 sept), to have a lower char-N to NO_x conversion than the other two chars, but a larger surface area for heterogeneous reduction also means a larger surface area for char-N oxidation or heterogeneous HCN release. The net effect is that the higher nitrogen, higher surface area Illinois #6 coal char yields apparent char-N to NO_x conversions which are greater than the other three Illinois #6 coal chars.

Two other observations should be made about the data in Figure 3-13. One, the results obtained with Ill (18 sept) char in both air and artificial oxidant are very similar. This similarity lends credibility to the both sets of data and verifies that firing conditions in artificial oxidant were close to those in air. Two, multiple data points were taken for some test conditions; based on these data points, the repeatability of the results is very good.

All data from initial NO_x experiments performed with Pittsburgh #8 coal chars and with Utah (13 sept) char are plotted in Figure 3-14. Except for the data points at 0 ppm initial NO_x collected in artificial oxidant, all the data were collected in air. Multiple data points were taken at only a few test conditions, but the repeatability is good for those cases where multiple data points exist. Also, the range of nitrogen contents of the chars is narrow (1.0-1.14%, dry basis), so the effect of nitrogen content on apparent char-N to NO_x conversion cannot be determined for this suite of Pittsburgh #8 coal chars.

Figure 3-15 contains data for both Knife River and Black Thunder coal chars taken in artificial oxidant and in air. All data points at 0 ppm initial NO_x were taken in Ar/CO₂/O₂ as were the data labeled “K. R. (26 oct)-Ar/15%CO₂/O₂” and K. R. (31 oct, 1 nov)-Ar/15%CO₂/O₂”; all other data were taken in air. Because only small amounts of these chars were collected, the number of test conditions was limited and very few data points were repeated. The nitrogen contents of the three chars shown in this plot are very low, ranging from 0.46% to 0.51%. Even with such low nitrogen contents, all three chars exhibit the strong dependence of apparent char-N to NO_x conversion on initial NO_x levels. Also, the apparent conversions in Figure 3-15 are similar to those for coal chars with much higher nitrogen contents. Implications of this result will be discussed in Section 4.0.

The range of conversions at any given NO_x level is large. For example, at 900 ppm initial NO_x, the char-N to NO_x conversion for Black Thunder char is 24% while that for K. R. (26 oct) char is close to 0%. When comparing the Knife River and Black Thunder coal char results, two possible sources of error should be considered. First, since conversion is

Figure 3-14. Influence of initial NO_x concentration and nitrogen content of the char on char-N conversion to NO_x for Pittsburgh #8 and Utah coal chars.

computed by dividing by the feed rate of char-N, small errors in measured NO_x levels will lead to greater errors in computed conversion with these low nitrogen chars than with the higher nitrogen bituminous coal chars. Second, since multiple data points were not taken, it is not clear how scattered the data for any particular char may be.

Several differences between the Black Thunder and Knife River chars might explain why char-N to NO_x conversions for Black Thunder char are higher than conversions for the Knife River chars at both 150 ppm and 900 ppm initial NO_x. First, the Black Thunder char is extremely burned out; carbon content (dry basis) is only 40% compared to 47% and 51% for the Knife River chars. Second, the particle size distribution (see Appendix C) of the Black Thunder char is much finer than that of either of the Knife River chars. Both small particle size and an open, porous structure resulting from a high degree of burnout could

Figure 3-15. Influence of initial NO_x concentration on char-N conversion to NO_x for Knife River and Black Thunder coal chars. Both air and artificial oxidant data are shown.

significantly affect whatever homogeneous and/or heterogeneous mechanisms were occurring.

Finally, there are large discrepancies between the air and the artificial oxidant data in Figure 3-15; conversions of char-N to NO_x in artificial oxidant are much higher than those in air. Since data are very sparse, it is unclear what conclusions can be drawn from these discrepancies.

In the previous section, the correlation between char-N conversion to NO_x at 0 ppm initial NO_x and nitrogen content of the char was not evident. Nevertheless, a correlation at high initial NO_x levels between nitrogen content and conversion for the Illinois #6 coal

chars was observed in Figure 3-13. As a result, data from all coal chars at high initial NO_x levels were replotted in Figure 3-16 and Figure 3-17 as apparent conversion of char-N to NO_x versus weight percent nitrogen in the char (dry basis) to check for a correlation. Figure 3-16 contains all data where initial NO_x levels were in the range of 404-453 ppm (dry basis) while Figure 3-17 contains all data where initial NO_x levels were in the 842-893 ppm range (dry basis). Only data in these narrow ranges were selected since the effect of initial NO_x level on apparent conversion is so pronounced.

The data in Figure 3-16 appear to be quite scattered although there is a general trend of increasing apparent conversion with increasing nitrogen content of the char. One of the

Figure 3-16. Apparent conversion of char-N to NO_x as a function of coal char nitrogen content for data taken with an initial NO_x concentration of 404-453 ppm.

outliers, the Utah char data point, can be explained based on the particle size distribution of the Utah char. This char has more particles which are greater than 106 μm in diameter than any other char. Large particle size will have an effect on diffusion of gaseous species and on heterogeneous reactions, which in turn will affect the conversion rates of char-N to NO_x.

The general trend in Figure 3-16 is seen again in Figure 3-17; as nitrogen content of the char goes up, so does the apparent conversion of char-N to NO_x. The data are not quite so scattered as those in Figure 3-16. The one major outlier is the Black Thunder char data point. As explained previously, the Black Thunder char had a higher degree of burnout and a much smaller particle size distribution than the other chars. Any NO reduction sites on the surface of the highly burned out Black Thunder char would be more widely dispersed in

Figure 3-17. Apparent conversion of char-N to NO_x as a function of coal char nitrogen content for data taken with an initial NO_x concentration of 842-893 ppm.

the ash matrix of the char, thus reducing the probability of NO encountering a reduction site and increasing the conversion of char-N to NO_x. Additionally, in Figure 3-16, the Utah char, with its particle size distribution skewed toward the larger diameters, produced char-N to NO_x conversions which were lower than other chars with similar nitrogen contents. In the case of the Black Thunder char data point in Figure 3-17, the small particle size distribution seems to produce the opposite effect; char-N to NO_x conversion increases.

If the data in these two figures are replotted versus nitrogen content on a dry, ash-free basis (daf), the general shape of the trends and the location of the outliers does not change significantly. Thus, the correlation between nitrogen content and char-N to NO_x conversion at these high initial NO_x levels appears to be significant.

Based on all these initial NO_x data, the conversion of char-N to NO_x is clearly a complex process which probably depends on the physical properties of particle size and pore structure, the chemical composition, and the interaction of diffusion and homogeneous and heterogeneous reaction mechanisms.

3.3.3 Influence of Flame Temperature at Various Initial NO_x Concentrations

Flame temperature data presented in the previous section (see “Importance of Local Flame Temperature” on page 34) indicated that local flame temperature had a small effect on char-N to NO_x conversions obtained with Ill (14,19,20,21 sept) char but no effect on conversions obtained with Pitt (19,24 oct) char. Since all of those data were taken in artificial oxidant where the initial NO_x level was essentially 0 ppm, it was unclear what effect flame temperature might have at other initial NO_x levels. Hence, a series of experiments was run with Pitt (19, 24 oct) char at initial NO_x levels which varied from 0 ppm to 900 ppm. Data were collected both in artificial oxidant and in air and with the electric heaters on and off.

The results of these experiments are plotted in Figure 3-18. Although there is no apparent effect of temperature at 0 ppm initial NO_x, at all other initial NO_x levels the apparent conversions of char-N to NO_x measured when the electric heaters were off are several percent lower than conversions measured when the electric heaters were on. Also, the data collected in artificial oxidant at an initial NO_x level of 900 ppm are lower than the corresponding air data in two of three cases. This could also be a temperature effect since the adiabatic flame temperature in artificial oxidant containing 25% CO₂ is 200 K lower than that in air. Lastly, it is interesting to note that at the 900 ppm initial NO_x level, the char-N to NO_x conversions are negative with the heaters turned off. This means a significant fraction of the initial gas phase NO_x is being reduced to N₂. From the standpoint of trying to reduce 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 opposite trend with temperature was seen in the previous Section 3.2 flame temperature data taken with Ill (14,19,20,21 sept) char in artificial oxidant; conversion actually increased as flame temperature decreased. However, these two opposite trends cannot be directly compared because the Ill (14,19,20,21 sept) char data were only collected at a 0 ppm initial NO_x condition.

3.3.4 Effect of O₂ Concentration

Since coal char is consumed primarily by oxidation reactions, it seems logical that O₂ concentration would play a significant role in char-N conversion to NO_x, whether the main reaction mechanisms are homogeneous or heterogeneous. In the previous section, the importance of O₂ concentration on char-N to NO_x conversion was studied by burning simulated coals from two different chars in artificial oxidant at various excess O₂ levels (see page 33). The conclusion was that char-N to NO_x conversion increased slightly as O₂ concentration was increased from 2% to 8%. However, only a few data points were taken because of the difficulty and expense of obtaining data in artificial oxidant. In order to clarify the role of O₂ concentration in char-N to NO_x conversion, more extensive testing was conducted burning the simulated coals in air with no NH₃ or NO doping. The problem with this nondoped air data is that the initial NO_x level, the result of thermal NO_x

Figure 3-18. Influence of local flame temperature on char-N to NO_x conversion of Pitt (19,24 oct) char at various initial NO_x levels in air and in artificial oxidant.

formation, decreased with increasing excess O₂ concentration and, as seen in Section 3.3.2, initial NO_x level has a strong effect on conversion.

To determine whether or not the effects of O₂ concentration on char-N to NO_x conversion were only an artifact of the changing initial NO_x concentration, all the data obtained from tests involving the variation of excess O₂ concentration were plotted in Figure 3-19 as apparent conversion versus initial NO_x concentration. O₂ concentrations for this range of initial NO_x concentrations fell between 1.75% and 8.25%, although O₂ concentration is ignored in this plot format.

A comparison of Figure 3-19 to the initial NO_x data plotted in Figure 3-12 reveals that the effect of O₂ concentration on conversion is not just an artifact of the changing initial NO_x levels. In Figure 3-12, the largest drop in conversion of char-N to NO_x going from an initial NO_x level of 0 ppm to 150 ppm is approximately 15%. In Figure 3-19, conversion for Ill (14,19,20,21 sept) char drops approximately 36% going from an initial NO_x level of 40 ppm to 160 ppm and conversion for Pitt (25,26,29 sept) char drops by 22% going from an initial NO_x level of 50 ppm to 180 ppm. All the other chars exhibit similar behavior. The fact that these drops in conversion are larger than 15% over a narrower range of initial NO_x concentration than 0-150 ppm indicates that variation of excess O₂ has an effect on char-N to NO_x conversion that is not just limited to the change it produces in initial NO_x.

Figure 3-19. Apparent char-N to NO_x conversion data from experiments where excess O₂ ranged from 1.75-8.25% plotted as a function of initial NO_x level.

levels. This conclusion agrees with the conclusion reached based on the excess O₂ data obtained in artificial oxidant.

All simulated coal data obtained from excess O₂ experiments conducted in air are plotted in Figure 3-20 as NO_x concentration measured in the exhaust (corrected to 3% excess O₂) versus excess O₂ measured in the exhaust. The same data are also plotted in Figure 3-21 as apparent conversion of char-N to NO_x versus excess O₂. For most of the chars in Figure 3-20, overall NO_x levels vary only slightly over the range of excess O₂ concentrations tested. This occurs because as O₂ concentration increases, initial NO_x levels decrease due to a decrease in thermal NO_x production; at 2% excess O₂, the exhaust NO_x concentration corrected to 3% excess O₂ (CFR method) is 195 ppm while at 8% excess O₂, it drops to 80 ppm. At the same time, char-N to NO_x conversion increases, resulting in a small net change in overall NO_x concentration.

In Figure 3-21, the general trend for all chars is that as excess O₂ concentration increases, conversion of char-N to NO_x increases. This trend contradicts the observations of Tullin et al. (1993b) and Goel et al. (1994) in their single particle fluidized bed experiments. They observed that as O₂ concentration was raised, the NO yields fell and the N₂O yields rose. Since N₂O is rapidly destroyed to form N₂ at pc conditions, a rise in N₂O yields at high O₂ concentrations would result in a drop in char-N to NO_x conversion, exactly opposite of the trends seen here.

Figure 3-20. Effect of excess O₂ level on measured exhaust NO_x concentration for various coal chars.

The data in Figure 3-20 and Figure 3-21 were separated by parent coal type for plotting in the next series of figures. Pittsburgh #8 and Utah coal char data are plotted together in Figure 3-22 and Figure 3-23. Also included in these figures for comparison are the excess O₂ data taken in artificial oxidant and shown previously in Figure 3-8; the data not specifically labeled as artificial oxidant data were taken in air. The NO_x concentration measured in the exhaust and corrected to 3% excess O₂ is plotted versus excess O₂ concentration in Figure 3-22 while the same data are plotted as char-N to NO_x conversion versus excess O₂ concentration in Figure 3-23.

With respect to Figure 3-22, the corrected exhaust NO_x concentration varies only slightly over the range of excess O₂ concentrations tested for data taken in air because of the balance between decreasing thermal NO_x and increasing char-N to NO_x conversion with increasing O₂ concentration. However, for the data taken in artificial oxidant, there is a steady increase in NO_x concentration with increasing excess O₂. This steady increase occurs because in the artificial oxidant flames, there is no decrease in thermal NO_x formation to counterbalance the increase in char-N to NO_x conversion.

In Figure 3-23, both air and artificial oxidant data exhibit a trend of increasing char-N to NO_x conversion with increasing O₂ concentration. However, the increase in conversion is much steeper for the air data than for the artificial oxidant data. As an example, for Pitt (25,26,29 sept) char burned in artificial oxidant, the conversion of char-N to NO_x increased

Figure 3-21. Effect of excess O₂ level on apparent conversion of char-N to NO_x for various coal chars. Initial NO_x varies from 42-176 ppm.

by 10% when excess O₂ concentration was increased by approximately 5%. For the same char burned in air, conversion increased by 22% when excess O₂ concentration was increased by 6%. The difference in slope between these two char-N to NO_x conversion curves for the same char is probably attributable to the effect of varying initial NO_x concentration on the data taken in air.

A further comparison of the Pitt (25,26,29 sept) char data taken in air and in artificial oxidant shows the magnitude of the effect of the initial NO_x level. At 2% excess O₂, the char-N to NO_x conversion in air exceeds that in artificial oxidant by more than 10%. This difference occurs because there is essentially 0 ppm initial NO_x in artificial oxidant while the initial NO_x level in air is 195 ppm (corrected to 3% excess O₂). As noted in section 3.3.2, there is a large drop in char-N to NO_x conversion going from 0 ppm to 195 ppm initial NO_x. At approximately 8% excess O₂, the initial NO_x level in air has dropped to 80 ppm (corrected to 3% excess O₂) with the artificial oxidant NO_x level again at 0 ppm, and the apparent conversions for the two different oxidants are almost the same.

All excess O₂ data from Illinois #6 coal chars are plotted in Figure 3-24. Data taken both in air and in artificial oxidant are included; the artificial oxidant data are labeled as such. As with the Pittsburgh #8 chars, a general trend of increasing char-N to NO_x conversion with increasing O₂ concentration is observed for both air and artificial oxidant data. However, the distinct difference between the slopes of the air and artificial oxidant curves observed with the Pitt (25,26,29 sept) char is not seen here. The Ill (16 oct) char data in artificial oxidant rise sharply between 2% and 5% excess O₂ and then drop off at 7%

Figure 3-22. Measured exhaust NO_x concentrations as a function of excess O₂ in both air and artificial oxidant for Pittsburgh #8 and Utah coal chars.

O₂. Because multiple data points were not taken, it is unclear whether or not the artificial oxidant trend is an experimental artifact, so no conclusions will be drawn from the shape of the artificial oxidant curve.

The last set of excess O₂ data, the Knife River char data, is seen in Figure 3-25. Only limited data were taken, but these data do show the same general trend as the other coal chars of increasing char-N to NO_x conversion with increasing O₂ concentration.

One final issue relating to excess O₂ concentration needs to be addressed, and that is the effect of temperature when changing O₂ concentration. As noted in Section 3.3.3, at initial NO_x levels greater than 0 ppm, the conversion of char-N to NO_x was reduced at lower flame temperatures. In the excess O₂ experiments, flame temperatures did drop as excess O₂ concentrations were increased as evidenced by the decrease in thermal NO_x formation with increasing O₂ concentration and by the temperature readings from the thermocouple located in port 1-1N. The effect of temperature on excess O₂ experimental results is not quantifiable, however, because no tests were run where O₂ and temperature were varied independently.

Nevertheless, a qualitative analysis can be made based on the data in Section 3.3.3 and in this section. As excess O₂ concentration is increased, flame temperature decreases. Since a reduced flame temperature was shown in the previous section to produce lower conversions of char-N to NO_x, the effect of flame temperature in the high excess O₂ cases

Figure 3-23. Apparent conversion of char-N to NO_x as a function of excess O₂ in both air and artificial oxidant for Pittsburgh #8 and Utah coal chars.

would be to reduce the conversion of char-N to NO_x. The fact that conversion actually increases with increasing excess O₂, the opposite of what the flame temperature effect would indicate, emphasizes that O₂ concentration plays a more important role than flame temperature in the oxidation reactions which are occurring.

3.3.5 Interaction of O₂ Concentration and Initial NO_x Levels

The interaction of O₂ and initial NO_x with char-N was studied using Ill (16 oct) char. In this series of experiments, measurements were taken at various initial NO_x concentrations at each of four excess O₂ levels: 2%, 3%, 5%, and 7%. The results are plotted in Figure 3-26 as apparent conversion of char-N to NO_x versus initial NO_x concentration (as measured) for each of the four O₂ levels. All NO_x data are from the FT-IR except for the 2% O₂ data point at 930 ppm initial NO_x, which was taken with the TECO analyzer.

It is immediately clear from Figure 3-26 that both O₂ and NO_x concentrations play significant roles in char-N conversion to NO_x. At all levels of initial NO_x tested, the percent conversion was highest for the 7% excess O₂ case and lowest for the 2% excess O₂ case. In fact, at the highest NO_x level tested (900 ppm), the char-N to NO_x conversion at 2% excess O₂ was negative. This same phenomenon was seen in Figure 3-18 for Pitt (19,24 oct) char when the electric heaters were turned off. A negative conversion indicates that NO_x levels actually decreased when char was added to the system.

Figure 3-24. Apparent conversion of char-N to NO_x as a function of excess O₂ in both air and artificial oxidant for Illinois #6 coal chars.

One conclusion from Figure 3-26 might be that initial NO_x concentration is more important than O₂ concentration. Why? At a given excess O₂ level, conversion of char-N to NO_x varies by more than 35% over the initial NO_x range tested while at a given initial NO_x level, conversion varies by less than 20% over the excess O₂ range tested. This conclusion may not be valid, however, because initial NO_x concentration was varied by a factor of nine while excess O₂ concentration was varied by a factor of approximately 2.5. Certainly, both gas phase NO_x and O₂ interact in important ways with char-N.

3.3.6 Influence of Char Loading at Various Initial NO_x Levels

The effect of the relative firing rates of char and natural gas on char-N to NO_x conversion is addressed in Appendix C. Based on data presented in Figure C.5 and Figure C.6, it was determined that over the range of natural gas and char firing rates tested, char-N conversion to NO_x was relatively unaffected by those firing rates. However, all those data were collected from simulated coal flames with no NH₃ or NO doping. Based on the importance of initial NO_x concentration in other coal char experiments, a series of experiments was run to study the interaction of char loading (i.e., char firing rate) and initial NO_x concentration.

The char used in these experiments was Pitt (25,26,29 sept). The char firing rate was varied from 2.05 kW to 8.8 kW and the initial NO_x concentration was varied from 0-900

Figure 3-25. Apparent conversion of char-N to NO_x as a function of excess O₂ for Knife River coal chars. All data were taken in air.

ppm with the 0 ppm initial NO_x data obtained from experiments in artificial oxidant. All other data were obtained in air. The natural gas firing rate was held constant at 24.9 kW. The data from these experiments are plotted in two different ways. In Figure 3-27, apparent conversion of char-N to NO_x is plotted versus initial NO_x concentration for five different char firing rates: 2.05 kW, 4.0 kW, 4.4 kW, 6.4 kW, and 8.8 kW. Although the data are sparse, several conclusions can be drawn. First, the effect of char loading is small under the conditions of these experiments. The char-N to NO_x conversions in the 100-150 ppm initial NO_x range are clustered between 30-40% and the conversions in the 900 ppm initial NO_x range are clustered between 0-10%. Second, although the effect is small, the conversion of char-N to NO_x increases as the char loading is increased.

In Figure 3-28, apparent conversion of char-N to NO_x is plotted versus the ratio of the char firing rate to the natural gas firing rate for five different initial NO_x ranges: 0 ppm, 85-110 ppm, 135-175 ppm, 440 ppm, and 880-900 ppm. In the initial NO_x range of 880-900 ppm, the small effect of increased char-N to NO_x conversion with increased char loading can again be seen. The main observation of this graph, however, is that over the range of char loadings tested, the initial gas phase NO_x concentration has a more significant impact on the overall char-N conversion to NO_x than does the char loading.

A final issue to consider with these data is that of temperature. Although flame temperature will increase as char loading is increased, the effect of flame temperature on the char loading results was probably very small. Why? The CFR method was used for all

Figure 3-26. Impact of excess O₂ and initial NO_x concentrations on the apparent conversion of char-N to NO_x for Ill (16 oct) char.

data points, which means that prior to adding char to the system, natural gas was fired with enough air to burn both the gas and the char. At the higher char firing rates, the higher required air flow rate cooled the furnace off slightly. When char was subsequently added to the system, flame temperatures did increase more at the higher char firing rates. But, when combined with the cooling effect, the overall result was that flame temperatures did not vary much over the range of char firing rates tested.

3.3.7 Comparison of Near Burner Data to Exhaust Data

In many of the experiments involving initial NO_x concentration, data were taken both at the exhaust (port 6-4W) and at port 1-1N, which is the first port below the burner. In this section, data taken at port 1-1 are plotted together with corresponding data from port 6-4 so that comparisons can be made. All experiments were conducted in air unless otherwise indicated. The plots in this section have the same axes: the y-axis is the change in measured NO_x concentration (dry basis) from that measured by the CFR method when firing natural gas alone to that measured when char is added to the system and the x-axis is the sampling location.

Data from simulated coal experiments with Nuchar at a high initial NO_x concentration (800 ppm) are found in Figure 3-29. At both ports 1-1 and 6-4, the measured NO_x concentration decreased when Nuchar was added to the system since, as shown in Figure 3-

Figure 3-27. Influence of initial NO_x level on apparent conversion of char-N to NO_x at various firing rates of Pitt (25,26,29 sept) char.

11, slight reduction levels of gas phase NO_x on the Nuchar surface were observed. Nevertheless, the measured decrease changes very little between ports 1-1 and 6-4, indicating that a only a very small amount of heterogeneous NO_x reduction on the Nuchar surface was occurring between the two sampling locations.

The Nuchar data can be compared to the data obtained from two of the Pittsburgh #8 coal chars; these data are presented in Figure 3-30 and Figure 3-31. In Figure 3-30, Pitt (27,28,29 sept) char data are plotted for three different initial NO_x levels; both NH₃ and NO were used as dopants. Unlike the Nuchar data, at all levels of initial NO_x tested, the measured NO_x concentration increased when char was added to the system. This increase occurred because, unlike the Nuchar, the Pitt (27,28,29 sept) char contains significant quantities of nitrogen which can be oxidized to form NO_x. What is interesting to note in Figure 3-30, however, is that at the highest initial NO_x level tested, the measured increase in NO_x concentration with the addition of char was much greater at port 1-1 than at port 6-4. This result is indicative that NO_x reduction reactions were occurring between ports 1-1 and 6-4 and contrasts with the Nuchar results where very little NO_x reduction occurred between the two ports. Similar results were obtained from tests with Pitt (25,26,29 sept) char.

Why is this effect seen at the highest initial NO_x levels only? Perhaps only high NO_x concentrations provide the driving force for whatever reduction reactions are occurring. This issue will be addressed in more detail in Section 4.0.

Figure 3-28. Influence of char firing rate on apparent conversion of char-N to NO_x at various levels of initial NO_x for Pitt (25,26,29 sept) char.

Data obtained from tests with Pitt (19,24 oct) char are graphed in Figure 3-31. Data were taken in air and in artificial oxidant (Ar/25%CO₂/O₂) with the electric heaters on and off in order to study the effect of local flame temperature on changes in NO_x concentration with the addition of char. Only the data taken at the highest initial NO_x level (850-900 ppm) are shown. Similar trends in air and in artificial oxidant data suggest that firing conditions in artificial oxidant were comparable to those in air.

The data from the tests run with the electric heaters on differ greatly from the data taken when the electric heaters were off. With the heaters on in both air and in artificial oxidant, the measured increase in NO_x concentration with the addition of char was much greater at port 1-1 than at port 6-4, an indication of NO_x reduction reactions occurring between the two sampling locations. The same result was observed for Pitt (27,28,29 sept) char in Figure 3-30. However, with the heaters off in both air and in artificial oxidant, the measured NO_x concentrations at both ports actually decreased with the addition of char. This decrease implies that NO_x reduction reactions between ports 1-1 and 6-4 can be significant and are enhanced at lower temperatures, perhaps because there is more nitrogen left in the solid phase at port 1-1; a similar conclusion was reached based on the data presented in Figure 3-18. The results with the heaters off are especially significant when one considers that any Pitt (19,24 oct) char which was not burned out by port 1-1 was a potential source of additional gas phase NO_x.

Figure 3-29. Change in measured NO_x concentration at ports 1-1 and 6-4 when Nuchar was added to a natural gas flame. Initial NO_x concentration was approximately 800 ppm.

Data obtained from Ill (14,19,20,21 sept) char are plotted in Figure 3-32. These data show trends similar to those seen with the Pitt (27,28,29 sept) char in Figure 3-30. At the highest initial NO_x level, the measured increase in NO_x concentration with the addition of char was much greater at port 1-1 than at port 6-4. In addition, the same effect, though not quite as large, appears at the middle initial NO_x level (450 ppm). Whatever NO_x reduction mechanism was occurring in the Pittsburgh #8 coal char tests appears to also be a factor with the Ill (14,19,20,21 sept) char.

Data from three Illinois #6 coal chars taken at the highest initial NO_x level (840-900 ppm) are compared in Figure 3-33. As noted on the graphs, the nitrogen content of the three chars varies from 1.61% to 1.13% by weight (dry basis). For the char with the highest nitrogen content, Ill (18 sept), the measured change in NO_x concentration with the addition of char was greater at port 6-4 than at port 1-1. In other words, a net production of NO_x occurred between the two ports. For the Ill (22 sept) char, the measured change in NO_x concentration with addition of char was slightly lower at port 6-4 than at port 1-1, which may mean that a very small quantity of NO_x was reduced between port 1-1 and port 6-4. For the char with the lowest nitrogen content, Ill (14,19,20,21 sept), the measured change in NO_x concentration after char addition was much greater at port 6-4 than at port 1-1, exactly opposite of the Ill (18 sept) char data but indicative that significant NO_x reduction reactions occurred between the front and back end ports.

Figure 3-30. Change in measured NO_x concentration at ports 1-1 and 6-4 when Pitt (27,28,29 sept) char was added to a natural gas flame. Tests were conducted at various levels of initial NO_x.

Hence, the Ill (14,19,20,21 sept) char exhibited a high NO_x reduction potential between ports 1-1 and 6-4, the Ill (22 sept) char exhibited a very low NO_x reduction potential between the same two ports, and the Ill (18 sept) char exhibited no NO_x reduction potential downstream of port 1-1. These results appear to correlate inversely with nitrogen content of the chars.

3.3.8 Parent Coal Experiments

Data from experiments conducted with the parent coals of the chars used in this study are included in this section for several reasons. First, the data may help to understand and interpret some of the char-N results. Second, the data illustrate some of the differences between the fate of volatile-N and the fate of char-N which have previously been addressed. Third, a comparison of the data to the results of other researchers may lend more credibility to the char-N data since both groups of experiments were run with the same equipment.

Details of how the coal experiments were run are found on page 198. Unless otherwise indicated, the coal firing rate was 29.3 kW, the overall stoichiometry was 1.15, and the oxidant was air. Four of the parent coals were tested: Pittsburgh #8, Utah, Illinois #6, and Knife River. Data obtained from burning all four coals in artificial oxidant (Ar/15% CO₂/O₂) are plotted in Figure 3-34 as conversion of fuel-N (volatile-N + char-N) to NO_x versus

Figure 3-31. Effect of flame temperature on changes in measured NO_x concentration when Pitt (19,24 oct) char was added to a natural gas flame. Oxidants were air and Ar/25%CO₂/O₂. Initial NO_x was 850-900 ppm.

weight percent nitrogen in the coal on a dry, ash free basis. Also included in this figure for comparison are data from work by Pershing et al. (1990). The data of Pershing et al. include a wide range of coals from lignites to anthracites and were collected in a 21 kW furnace mounted with a premixed burner. As with the present coal data, the data of Pershing et al. were obtained by burning the coals in an artificial oxidant mixture of Ar, CO₂, and O₂.

The present coal data fall within the range of data reported by Pershing et al. Consideration of the present coal data alone would indicate that conversion of fuel-N to NO_x increases with increasing nitrogen content of the coal. Nevertheless, when put in context with the much larger suite of coals tested by Pershing et al., it appears that such a correlation does not exist. It is interesting to note that when char-N to NO_x conversion data at high levels of initial NO_x were plotted versus nitrogen content of the char in Figure 3-16 and Figure 3-17, a rough correlation was observed, similar to the correlation seen here of the present coal data with nitrogen content of the coal.

The conversion of fuel-N to NO_x for all four coals is lower than the conversion of char-N to NO_x for the coal chars (see Figure 3-2). Fuel-N conversion to NO_x ranges from approximately 30% for the Knife River coal to approximately 36% for the Illinois #6 coal. The range of char-N conversions to NO_x was 38% to 61%. Thus, under the conditions of these experiments, the char-N has a greater tendency to form NO_x species than does the

Figure 3-32. Change in measured NO_x concentration at ports 1-1 and 6-4 when Ill (14,19,20,21 sept) char was added to a natural gas flame. Tests were conducted at various levels of initial NO_x.

Figure 3-33. Change in measured NO_x concentration at ports 1-1 and 6-4 when three Illinois #6 coal chars were added to a natural gas flame. Initial NO_x levels were 840-900 ppm.

Figure 3-34. Conversion of fuel-N to NO_x in artificial oxidant as a function of nitrogen content of the coal. Data from the present experiments and from Pershing et al. (1990) are included.

overall fuel-N (volatile-N + char-N), and the char-N to NO_x conversions vary over a much greater range than the fuel-N to NO_x conversions.

Perhaps a more accurate comparison would be between the conversion of fuel-N to NO_x and the conversion of char-N to NO_x at high initial NO_x levels (see Figure 3-12). In this comparison, char-N conversion to NO_x still varies over a greater range than fuel-N to NO_x conversion, but char-N conversion levels (16% to 34%) are, in general, lower than fuel-N conversion levels.

In addition, while the fuel-N to NO_x conversion of the Knife River coal is the lowest of the coals tested, the char-N to NO_x conversions of the Knife River chars were higher than any other chars at 0 ppm initial NO_x and the same as the other chars at 850 ppm initial NO_x.

(see Figure 3-2 and Figure 3-12). In contrast, Illinois #6 coal has the highest conversion of fuel-N to NO_x, while its chars are just behind Knife River and Black Thunder chars in terms of char-N conversion to NO_x at 0 ppm initial NO_x. All these differences emphasize the fact that there are many factors which must be accounted for when modeling the fate of volatile-N and of char-N which greatly influence the outcome. In the case of char-N, an important factor is the interaction of gas phase species with the char. If the contribution of char-N to the total NO_x present in a coal flame is to be accurately predicted, these interactions must be correctly modeled.

The effects of O₂ concentration on the conversion of fuel-N to NO_x for each of the four coals are seen in Figure 3-35 through Figure 3-38. In these experiments, multiple data points were taken at five different excess O₂ levels ranging from 2% to 9%. These multiple data points represent both data taken on different days and data taken at different times on the same day. All of the data were taken while burning coal in air, so the measured NO_x concentrations include the contributions of both thermal NO_x and fuel NO_x. Since there was no way to accurately determine the contribution of thermal NO_x to the total NO_x measured, the data on all four plots are reported as measured exhaust NO_x (rather than fuel-N conversion to NO_x) versus measured excess O₂. All measured NO_x concentrations are corrected to 3% excess O₂.

Figure 3-35 contains all data taken while firing Pittsburgh #8 coal. Although there is considerable scatter in the data, there is a general trend of increasing NO_x levels with increasing excess O₂ concentration. This same trend is seen for all four coals, including Utah coal in Figure 3-36, Illinois #6 coal in Figure 3-37 and Knife River coal in Figure 3-38. The scatter in the data on all the plots is most likely due to temperature. During the course of a day's experiments when excess O₂ concentration was varied from 2% to 9% and then back to 2%, temperatures in the furnace dropped considerably between the first and second 2% excess O₂ points due to the cooling effect of the high excess air levels. As an example, NO_x concentrations for Illinois #6 coal at 2% excess O₂ were measured an hour apart with higher excess O₂ cases being run in between. The measured NO_x concentration the first time was 1262 ppm and the thermocouple in port 1-1 N read 1692 K; an hour later, the measured NO_x concentration was 1204 ppm and the same thermocouple read 1642 K.

The trend in all four plots of an increase in measured NO_x concentration with increases in excess O₂ has been reported by other researchers including Pershing et al. (1990). According to Pershing et al., in premixed coal flames there is a very slight increase in fuel-N to NO_x conversion with excess O₂, but most of the increase in NO_x concentration with excess O₂ is attributable to thermal, not fuel, NO_x. Hence, under premixed, excess O₂ conditions, the effect of O₂ concentration on fuel-N conversion to NO_x is probably less than its effect on char-N to NO_x conversion.

A comparison of data taken in air to data taken in artificial oxidant is seen in the last series of coal plots. Figure 3-39 contains data from Pittsburgh #8 coal experiments, Figure 3-40 from Illinois #6 coal experiments, and Figure 3-41 from Knife River coal

Figure 3-35. Effect of O₂ concentration on NO_x formation in Pittsburgh #8 pulverized coal flames.

Figure 3-36. Effect of O₂ concentration on NO_x formation in Utah pulverized coal flames.

Figure 3-37. Effect of O₂ concentration on NO_x formation in Illinois #6 pulverized coal flames.

Figure 3-38. Effect of O₂ concentration on NO_x formation in Knife River pulverized coal flames.

experiments. The artificial oxidant data were taken in mixtures of 0%, 15% and 25% CO₂ with O₂ held constant at 21% and the balance made up by Ar; the majority of data were taken in a 64% Ar/15% CO₂/21% O₂ mixture. Excess O₂ measured in the exhaust was approximately 3.2% ($\pm 0.4\%$) for both artificial oxidant and air data. For each coal, both air and artificial oxidant the data are plotted as NO_x measured in the exhaust versus the temperature measured by the thermocouple probe located in port 1-1N.

Figure 3-39. Influence of local flame temperature on NO_x formation in Pittsburgh #8 pulverized coal flames. Both air and artificial oxidant data are included.

Based on the Pittsburgh #8 coal data plotted in Figure 3-39, both the air and the artificial oxidant data are correlated by local flame temperature, i.e., there is a general trend of increasing NO_x levels with increasing temperature measured by the thermocouple probe. This observation confirms that the scatter in the excess O₂ data in Figure 3-35 through Figure 3-38 was primarily due to temperature fluctuations in the furnace.

The Illinois #6 coal data plotted in Figure 3-40 and the Knife River coal data plotted in Figure 3-41 also appear to be well correlated by the port 1-1N thermocouple probe temperature; NO_x concentration in the exhaust increases with increasing temperature. Thus, the effect of temperature on overall NO_x production is not coal type dependent for the small suite of coals tested.

The increases in measured NO_x levels with temperature are not just a result of increased thermal NO_x production, as evidenced by the artificial oxidant data where no thermal NO_x was present. This conclusion is supported by the experimental results of Pershing et al. (1990). Pershing and coworkers conducted experiments with lignite,

Figure 3-40. Influence of local flame temperature on NO_x formation in Illinois #6 pulverized coal flames. Both air and artificial oxidant data are included.

Figure 3-41. Influence of local flame temperature on NO_x formation in Knife Rive pulverized coal flames. Both air and artificial oxidant data are included.

bituminous, and subbituminous coals in artificial oxidant and saw increases in NO_x levels of up to 700 ppm for a 500 K increase in theoretical adiabatic flame temperature.

The temperature trends in the coal data correlate well with the char data presented in Figure 3-18. In that figure, a decrease in char-N conversion to NO_x with decreasing local flame temperature was observed only at the higher initial NO_x levels, but it is those higher initial NO_x levels which most accurately simulate the high NO_x levels seen in these coal flames.

In conclusion, experimental results from both char-N and parent coal experiments have been included in this section and observations regarding the results have been made.

4.0 Single Particle Model for NO_x Formation During Pulverized Coal Combustion

In order to obtain a better understanding of the process of NO_x production at PC conditions, a single particle model for the heterogeneous formation of NO_x during coal combustion has been developed. Several models have been developed as part of this program, with different degrees of approximation. In this section the analytical model which is the easiest to adapt to a CFD code is implemented and compared, first with the numerical results of Visona and Stanmore (1996).

4.1 Governing Equation

Assuming the char particle as a sphere and considering pseudo-steady state and constant effective diffusivity, the equation which represents the mass balance for each species i is:

$$\frac{-D_e}{r^2} \frac{d}{dr} \left(r^2 \left(\frac{dC_i}{dr} \right) \right) = R_i^v \quad (1)$$

where r : radial position (m), D_e : effective diffusivity (m² s⁻¹), C_i : concentration of species i (mol m⁻³) and R_i^v : volumetric reaction rate (mol m⁻³ s⁻¹)

With the following boundary conditions:

$$\text{At } r = 0, C_i \text{ is finite} \quad (2)$$

At $r = R_p$,

$$D_e \left. \frac{dC_i}{dr} \right|_{r=R_p} = k_g (C_i^b - C_i^s) \quad (3)$$

Where R_p : radius of the particle (m), k_g : mass transfer coefficient (m s⁻¹), C_i^b : concentration of species i in the bulk (mol m⁻³), C_i^s : concentration of species i at $r = R_p$ (mol m⁻³).

4.2. Reactions.

The model considers the following heterogeneous reactions:

- Carbon oxidation:

- NO formation:

- NO reduction:

This is a simplification selected because it provides a good approximation that provides a realistic representation of the major trends in the data (Visona and Stanmore, 1996). Here only the CO production by char oxidation was considered, neglecting the production of CO₂ which is known to be important at lower temperatures. NO is considered to be only reduced by the char surface, although it known that CO enhances NO reduction. And NO is considered to be the exclusive product of char-N oxidation, neglecting the production of HCN or N₂O which have been observed in selected experiments.

Since at high temperatures encountered in PC combustors the carbon oxidation is more likely to produce CO than CO₂ the first assumption is not expected to introduce a significant error. Also the N₂O production at PC conditions is very low compared to the NO yield.; but its neglect could change the reaction pathway and will therefore have subtle effects on the functional dependence of NO production on combustion conditions. The assumption with highest influence on the results is expected to be the neglect of the role of CO in augmenting the NO/char reduction reaction.

The model leads to the following rate expressions:

$$R_{O_2}^v = -k_{O_2} C_{O_2} \quad (7)$$

$$R_{NO}^v = \frac{1}{\nu_{O_2}} \left(\frac{N}{C} \right) k_{O_2} C_{O_2} - k_{NO} C_{NO} \quad (8)$$

In the derivation of the rate expression for NO formation, it was assumed that the oxidation rate for nitrogen is equal to the oxidation rate of carbon times N/C, where N/C is the nitrogen to carbon atomic ratio for the char. N/C is assumed constant through the process of char combustion. k_{O_2} is the rate coefficient for carbon (s⁻¹), k_{NO} for NO reduction on the char surface and $\nu_{O_2} = 0.5$ is the stoichiometric coefficient for carbon-oxygen reaction.

4.3. Analytical Solution.

In this study, equation (1) is solved for O₂ and NO. The analytical solution, is presented next.

4.3.1 Oxygen

For oxygen, $R_i^v = -kC_i$ and a solution to equation (1) is:

$$C_{O_2} = \frac{c_1}{r} \sinh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) + \frac{c_2}{r} \cosh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) \quad (9)$$

C_2 may be eliminated by applying the boundary condition (2). Equation (9) then becomes:

$$C_{O_2} = \frac{c_1}{r} \sinh\left(\left(\frac{k_{O_2}}{D_e}\right)^{1/2} r\right) \quad (10)$$

Or in dimensionless form:

$$C_{O_2} = \frac{c_1}{R_p} \frac{\sinh(\phi_{O_2} \xi)}{\xi} \quad (11)$$

Where c_1 is a constant evaluated from the boundary condition (3):

$$\frac{c_1}{R_p} = \frac{Sh C_{O_2}^b}{\sinh(\phi_{O_2}) (Sh + \phi_{O_2} \coth \phi_{O_2} - 1)} \quad (12)$$

$\phi_{O_2} = \left(\frac{k_{O_2}}{D_e}\right)^{1/2} R_p$ and $Sh = \left(\frac{k_g}{D_e}\right) R_p$ are modified Thiele and Sherwood numbers, respectively,

and $\xi = r / R_p$ is the dimensionless radius.

4.3.2 Nitric Oxide (NO)

An analytical solution of equation (1) is:

$$C_{NO} = \left\{ \frac{1}{\xi(\phi_{O_2}^2 - \phi_{NO}^2)} \right\} \left\{ -c_3 \sinh(\phi_{O_2} \xi) - B_1 (\phi_{NO}^2 \sinh(\phi_{NO} \xi) - \phi_{O_2}^2 \sinh(\phi_{NO} \xi)) \right\} \quad (13)$$

Where $c_3 = \frac{1}{v_{O_2}} \left(\frac{N}{C} \right) \left(\frac{c_1}{R_p} \right) \phi_{O_2}^2$ is a constant, B_1 and B_2 are integration constants and

$\phi_{NO} = \left(\frac{k_{NO}}{D_e}\right)^{1/2} R_p$ is the modified Thiele modulus for NO.

By applying the boundary conditions (2) and (3) one can simplify equation (13) to:

$$C_{NO} = c_4 \frac{\sinh(\phi_{O_2} \xi)}{\xi} + c_5 \frac{\sinh(\phi_{NO} \xi)}{\xi} \quad (14)$$

With:

$$c_4 = \frac{c_3}{(\phi_{NO}^2 - \phi_{O_2}^2)} \quad (15)$$

$$c_5 = \frac{(\phi_{O_2}^2 - \phi_{NO}^2)C_{NO}^b Sh + c_3 [\phi_{O_2} \cosh(\phi_{O_2}) - \sinh(\phi_{O_2})] + c_3 Sh \sinh(\phi_{O_2})}{(\phi_{O_2}^2 - \phi_{NO}^2) \{ Sh \sinh(\phi_{NO}) + [\phi_{NO} \cosh(\phi_{NO}) - \sinh(\phi_{NO})] \}} \quad (16)$$

4.4. Mass Transfer and Kinetic Parameters.

In order to determine the NO and O₂ concentration profiles it is necessary to find the kinetics and mass transfer parameters needed in the analytical solutions given above. In order to compare the analytical solution with Visona and Stanmore's numerical results (1996), we used the same parameters as they used as shown in the next section.

4.4.1 Mass transfer parameters.

Effective diffusivity D_e (m² s⁻¹):

$$\frac{1}{D_e} = \frac{1}{D_{knud}} + \frac{1}{D_{bulk}} \quad (17)$$

Where $D_{knud} = \frac{24.25 \epsilon^2 T^{0.5}}{A_p \rho_p}$ is de Knudsen diffusivity and $D_{bulk} = 1.28 \times 10^{-9} T^{1.75}$ is the bulk diffusivity. A_p (particle surface area) = 20000 m² kg⁻¹, ϵ (char porosity) = 0.41 (-), and ρ_p (particle density) = 1250 kg m⁻³. Finally: $k_g = \frac{D_{bulk}}{R_p}$ is the mass transfer coefficient (m s⁻¹).

4.4.2 Reaction rates.

The carbon oxidation from Smith (1978) is used:

$$k_{O_2} = A_{O_2} \exp\left(\frac{-E_A}{RT}\right) \frac{RT A_p \rho_p}{M_C} v_{O_2} \quad (18)$$

Where k_{O_2} (s⁻¹) is the reaction coefficient for carbon oxidation, $A_{O_2} = 3.01 \times 10^{-2}$ (kgC m⁻² s⁻¹ Pa⁻¹) is the pre-exponential factor, $E_A = 179.4 \times 10^3$ (J mol⁻¹) is the activation energy, R is the universal gas constant in (J mol⁻¹ K⁻¹), T is the temperature (K), and M_C is carbon molecular weight (kg mol⁻¹).

For NO reduction the reaction rate constant of Chan et al (1983), recommended by Visona and Stanmore (1996), is used:

$$k_{NO} = A_{NO} \exp\left(\frac{-E_A}{RT}\right) RT p_p \quad (19)$$

For this reaction $A_{NO}=3.138 \times 10^4$ (mol NO kg⁻¹ s⁻¹ Pa⁻¹), $E_A = 183.0 \times 10^3$ (J mol⁻¹).

4.5. Test Parameters:

The same parameters as those considered by Visona and Stanmore (1996) are used:

$\frac{N}{C}$: Nitrogen to carbon atomic ratio in char:

1750 K: (1.0/78.9)(12/14)=0.0109 atoms N/atoms C

1250 K: (1.1/69.9)(12/14)=0.0135 atoms N/atoms C

R_p : Radius of the particle (m): 19×10^{-6}

T=1250, 1500, 1750 K

C_{NO}^b =0 - 1500 ppm

$C_{O_2}^b$ =20% v

4.6. Comparison of the Model to Visona and Stanmore's Calculations.

The model previously outlined was compared to Visona and Stanmore's single particle model (1996). Although Visona and Stanmore's approach is mostly the same as the present study, two main differences should be noticed:

- In contrast to the pseudo steady state approximation used in this study, Visona and Stanmore treated the mass balance equation as time dependent:

$$\frac{\partial C_i}{\partial t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C_i}{\partial r} \right) = R^v \quad (20)$$

- In contrast to the treatment in the analytical model of the effective diffusivity D_e , the particle surface area A_p , and the char porosity ϵ as constant during the char burn-out process, Visona and Stanmore allowed for the variation of these properties.

These two distinctions should be taken into account when comparing the results of the analytical model (present work) and the numerical model (Visona and Stanmore).

Figure 4.1 shows the NO concentration profile within a 38μm particle, at 1750 K, with C_{NO}^b =1000 ppm and at $C_{O_2}^b$ = 20%. Only the NO reduction was considered, this means that the

source terms were switched off. The results from both models are alike, however a slight tendency for lower NO reduction is seen for the analytical solution. This may be explained since Visona and Stanmore's data are for 10% burnout, where their model predicts higher char surface area. This will imply faster NO reduction and therefore the depletion of NO will occur at higher values of r/R .

Figure 4.1. NO concentration profiles within the particle. Particle size = 38 μ m, T = 1750 K, C_{NO}^b = 1000 ppm, $C_{O_2}^b$ = 20%. Only NO reduction is considered.

Figure 4.2 shows the NO profile when only NO production is considered. Although both models predicts the same trend, there is considerably disagreement in the concentration at $r=0$ for high temperatures (at 1250 K both lines coincide). The difference in the physical properties do not explains the discrepancy between the models, since it only explains slight differences in the slope of the lines, but not on the final value.

A convincing reason that explains why both models predicts the same profile at 1250 K whereas at 1750 K they are off by a factor of 1.8 was not found. The main parameters associated with NO concentration in the center of the particle are $\frac{N}{C}$ (the Nitrogen/Carbon atomic ratio of the char) and ν_{O_2} , the stoichiometric coefficient for carbon-oxygen reaction (mol O₂ mol C⁻¹). Both parameters may vary with temperature. Although in this study the same parameters as those of Visona and Stanmore (1996) were used, an increase on ν_{O_2} , or a decrease on $\frac{N}{C}$ will lead to agreement between both models.

Figure 4.2 NO concentration profiles within the particle. Particle size = 38 μ m, $T = 1750$ K, $C_{NO}^b = 0$ ppm, $C_{O_2}^b = 20$ % Only NO production is considered.

Figure 4.3 presents once more the comparison between the two models, but when both, NO production and reduction were considered. As may be expected, though both models predicts similar trends, there is considerable discrepancy in the absolute values. The explanation for the difference may be a combination of the two previously stated: different physical properties, as well as a different interpretation on $\frac{N}{C}$ or v_{O_2} values. However the real influence of these differences should be considered not only in the NO concentration profile within the particle, but also in the fractional conversion of char-N to NO as will be further discussed.

Figure 4.3. NO concentration profiles within the particle. Particle size = 38 μ m, T = 1750 K, $C_{NO}^b = 0$ ppm, $C_{O_2}^b = 20$ %. NO production and reduction considered.

4.7. Instantaneous and Net Conversion of Char Nitrogen to NO.

Once the NO concentration profile within the particle was determined, the conversion of char-N to NO was computed. The O_2 concentration profile inside the particle was used to determine the conversion vs. time plot. Assuming a shrinking core model:

$$t = -\frac{\rho_p \nu_{O_2} C}{D_e M_c} \int_{R_p|_{t=0}}^{R_p} \frac{1}{\left. \frac{dC_{O_2}}{dr} \right|_{r=R_p}} dR_p \quad (21)$$

Where C is the mass fraction of carbon in the char, $\left. \frac{dC_{O_2}}{dr} \right|_{r=R_p}$ is determined from Equation (10)

and the char conversion x is:

$$x = \frac{R_p^3 - R^3}{R_p^3} \quad (22)$$

Hurt has experimentally found for a 106-125 μ m particle, at $C_{O_2}^b = 12\%$ and temperatures between 1600-1900 K, that 117 ms were needed to obtain a char conversion of 28%. The present model predicts 103 ms are needed for 28% of conversion at a temperature of 1750K, $C_{O_2}^b = 12\%$ and for a particle of 110 μ m of diameter. For this set of conditions the model gives a fair representation of the experimental burnout.

The differential conversion of char-N to NO, f_{NO} was defined as the ratio between the rate at time t of at which moles of NO leave a particle, and the rate at which moles of NO would leave the particle if all char-N were converted to NO, or:

$$f_{NO} = \frac{-4\pi R_p^2 D_e \left. \frac{dC_{NO}}{dr} \right|_{r=R_p}}{\frac{4\pi R_p^2 D_e \left(\frac{N}{C} \right) \left. \frac{dC_{O_2}}{dr} \right|_{r=R_p}}{\nu_{O_2}}} \quad (23)$$

The integral conversion of char-N to NO, F_{NO} represents the ratio between the cumulative moles of NO that leave the particle and the total moles of NO that would have left the particle if all char-N were converted to NO.

$$F_{NO} = \frac{-\int_0^t 4\pi R_p^2 D_e \left. \frac{dC_{NO}}{dr} \right|_{r=R_p} dt}{\frac{4}{3}\pi \left(R_p \Big|_{t=0} \right)^3 \left(\frac{N}{C} \right) \frac{\rho_p C}{M_C}} \quad (24)$$

Figure 4. 4 presents the integral char-N conversion to NO vs. char burn-off. The analytical solution predicts almost the same results as those of Visona and Stanmore. The similarity between both lines suggests that the differences between both models, observed in the NO concentration within the particle, may not be so important when considering the char-N

conversion to NO. In fact, from equation (24) it is clear that the value of $\left. \frac{dC_{NO}}{dr} \right|_{r=R_p}$ is what

determines the total char-N to NO conversion, and from Figure 4.3 we may see that this value (the slope of the C_{NO} vs. r/R curve) is very similar for both models. The slight discrepancy between both models is more likely due to the fact that Visona and Stanmore considered non-stationary state as well as variable physical properties.

Figure 4. 4. Integral Char-N to NO conversion $T = 1750K$, $C_{NO}^b = 0$, $C_{O_2}^b = 20\%$.

Particle size = $38\mu m$.

The differential char-N conversion to NO is presented Figure 4.5. Although Visona and Stanmore did not present this type of data for their model, a similar trend has been experimentally found by Goel et al (1994) for combustion in a fluidized bed and modeled by the same author at pulverized coal combustion. However in their model, Goel et al did consider N₂O formation, so comparison is not completely valid.

Figure 4.5. Differential char-N conversion to NO. $T = 1750\text{K}$, $C_{NO}^b = 0$, $C_{O_2}^b = 20\%$. Particle size = $38\mu\text{m}$.

Visona and Stanmore (1996) also analyzed the influence of NO bulk concentration on char-N conversion to NO (Figure 4.6). Both models predicts a decrease in the integral char-N conversion to NO when C_{NO}^b is increased. However Visona and Stanmore's model predicts a higher influence of the bulk concentration on the char-N conversion to NO. Visona and Stanmore's results are only reported at $T = 1250\text{ K}$. Just for comparison, the analytical results at 1750 K are also included.

The effect of particle size is shown by Figure 4.7. Both models predict in a very similar way a reduction of the char-N conversion to NO as particle size is increased. It should be noticed that the difference between both models is greater when analyzing the influence of NO bulk concentration, than when analyzing the particle size's influence. The fact that Visona and Stanmore considered variable mass transfer properties, as well as a non steady state seems to be the most probable reason for this discrepancy.

Figure 4.6. Variation of the char-N conversion to NO with the NO bulk concentration.
Particle size = $38\mu\text{m}$, $C_{O_2}^b = 20\%$

Figure 4.7. Variation of the char-N conversion to NO with the particle size.
 $T = 1750\text{ K}$, $C_{O_2}^b = 20\%$, $C_{NO}^b = 0$

So far we may conclude that a single particle model for the NO formation at PC combustion conditions was developed based on an analytical solution of the mass transfer balance equation. This model predicts similar trends and results as Visona and Stanmore's single particle model. There are some differences between both model predictions which may be mainly explained due to the fact that Visona and Stanmore considered variation in the physical properties with time, whereas the present study did not.

Clearly further work is needed to determine the differences observed with Visona and Stanmore's calculations but these differences were small enough that the analytical model was considered to be adequate for use in a first approach in the interpretation of Spinti's (1997) results presented earlier in this report.

4.8. Application of the Model to Data from Spinti (1997).

The use of low particle load (less than 1% by volume) suggests that a particle model, as that previously described, may succeed in modeling Spinti's data (1997) presented earlier in Section 3.0 of this report. The model's main assumptions, pseudo-steady state, only CO production during char oxidation, and NO reduction happening only on char surface seem probable considering the high temperature of Spinti's experiments (above 2200 K) and the simulated coal environment.

The chars used by Spinti had higher ash content and lower carbon content than the chars used in most char-NO reduction studies (Table 4.1). Therefore, the first step in order to model Spinti's results, was to determine the value of k_{NO} (the constant for the NO reduction reaction).

Table 4.1. Summary of Char-N conversion to NO_x from some references.

Ref.	Char source	Ash (%)	in C ^a (%) in char
Spinti (1997)	29 kW PC furnace. O ₂ . T=2200-2400K	17.8 - 56.2	40 - 69
Pershing and Wendt (1977)	Gasification Process	20.8	72.8
Wang et al (1994)	N ₂ EFR ^b T=1273 K	2.1-18.4	77.9 - 93.1
Song et al (1982)	He. Drop tube reactor. T=1250, 1750 K.	12.1-18.0	69.9 - 78.0
Chan et al (1983)	Fixed bed reactor. He. T=1273K	14.0	80.5
De Soete (1990)	Ar 1500K	N.A.	82.8 - 88.6
Wang et al (1996)	He. Wire mesh reactor. T=1000-1800 K.	N.A.	80.5 - 97.4

^a Ultimate analysis (dry)

^b EFR: Entrained Flow Reactor

4.8.1 Parameter Estimation.

The reaction rate constant k_{NO} was determined from a least square optimization of Spinti's (1997) results. The minimized function, was defined by:

$$\zeta = \sum_{i=1}^N (F_{NO}^{\text{exp}} - F_{NO}^{\text{model}})_i^2 \quad (25)$$

Where N is the total number of data points, and F_{NO}^{exp} and F_{NO}^{model} the experimental and model predicted net char-N conversion to NO. Due to the reduced number of data points reported by Spinti (four points for each char at one temperature), k_{NO} was considered as a whole, and it was not separated into a pre-exponential factor and an activation energy.

The only parameter which was allowed to vary was k_{NO} , all other parameters were found from Spinti's experimental data or assumed to be similar to those reported in the literature. Table 4. 2 presents a brief description of the source of the main parameters used in the model.

Table 4. 2. Parameters used during k_{NO} determination

PARAMETER	SOURCE	Comments
Char oxidation constant	Smith's value, as described by Visona and Stanmore (1996)	
Effective Diffusivity, mass transfer coefficient	Visona and Stanmore (1996)	The pseudo-steady approach did not consider time variation of these properties
O ₂ bulk concentration	Spinti's (1997) reported data (3%)	
Particle density	Visona and Stanmore (1996)	Not reported by Spinti (1997)
Particle diameter	Spinti's (1997) experimental particle size distribution.	$D_p = \int_0^1 D_p(x) dx$
Particle surface area	Spinti's experimental N ₂ values (1997).	When available, when not, average of chars
Porosity	Visona and Stanmore (1996)	Not reported by Spinti (1997).
Pressure	Spinti's measurements (0.84 atm) (1997)	
Temperature	Spinti's measurements (1997)	The temperature of port 1 were considered since it is where combustion takes place.
Ultimate analysis	Spinti's experimental values (1997)	

Figure 4.8 to Figure 4.10 represent char-N conversion to NO_x for three different parent coals. The most remarkable trend is the decrease in conversion as NO bulk concentration is increased. This decrease can be split in two regions. At low NO bulk concentration, there is a higher negative slope in the F_{NO} vs. NO bulk concentration curve. This slope becomes less negative, as NO bulk concentration is increased.

Figure 4.8. Char-N conversion to NO_x for Illinois #6 chars. Data from Spinti (1997).

Figure 4.9. Char-N conversion to NO_x for Knife River chars. Data from Spinti (1997).

Figure 4.10 Char-N conversion to NO_x for Pittsburgh %8 chars. Data from Spinti (1997).

Figure 4.11 - Figure 4.13 provide comparisons between model and experimental results for one char of each different parent coal. Although the model predicts the same trend of experimental results, it fails in predicting the change in slope already explained. In all but one of the Figures there is acceptable agreement between model and experimental data for NO bulk concentrations lower than 400 ppm, however the model underpredicts the conversion at high NO concentrations.

Figure 4.11. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased.

Illinois #6, Sept. 14,19,20,21. $k_{NO} = 5.10 \times 10^7 \text{ s}^{-1}$

Figure 4.12. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased.

Knife River, Oct. 31, Nov. 1. $k_{NO} = 1.51 \times 10^7 \text{ s}^{-1}$

Figure 4.13. Comparison between experimental and model predictions of char-N conversion to NO as NO bulk concentration is increased. Pittsburgh#8 Sept. 25,26,29. $k_{NO} = 1.96 \times 10^7 \text{ s}^{-1}$

The influence of some parameters in the optimization process is shown in Figure 4.14-Figure 4.17. As it can be seen, the optimization process is not very sensitive to changes on each of the tested parameters. Although there is a slight change in the slope when some parameters (temperature and particle radius mainly) are changed, it seems unlikely that variations on any of these parameters, between reasonable values, is responsible for the change in slope observed at high NO bulk concentrations.

Figure 4.14 Effect of particle radius on optimization results. Illinois#6. Sept. 14,19,20,21.

Figure 4. 15. Effect of temperature on optimization results. Illinois#6. Sept. 14,19,20,21.

Figure 4. 16. Effect of char surface area on optimization results. Illinois#6. Sept. 14,19,20,21

Figure 4.17. Effect of char porosity on optimization results.
Illinois#6. Sept. 14,19,20,21

The effect of k_{NO} in the char-N to NO conversion is presented in Figure 4.18. Higher values of k_{NO} imply lower F_{NO} when the bulk NO concentration is zero. They also imply a greater negative slope.

Figure 4.18. Effect of k_{NO} in the model predictions. Illinois#6. Sept. 14,19,20,21

Since the model cannot predict the change in slope at high concentrations, the optimization was repeated to fit the data only at the lower concentrations that are of importance for the current generation of low NO_x boilers. Figure 4. 19 presents the comparison between model and experimental results when only the three points at low NO bulk concentrations were considered. There is an improvement for all chars, and for some chars the lines predicted by the model are almost identical to experimental values.

Figure 4. 19. Comparison between experimental and model predictions (only first three points considered in optimization process).

Illinois #6, Sept. 14,19,20,21. $k_{NO} = 6.26 \times 10^7 \text{ s}^{-1}$

4.8.2 Relation Between k_{NO} and Char Properties.

In order to verify the validity of the model, the values of k_{NO} determined by the least square minimization were compared to those of Chan et al (1983). Figure 4.20 presents the ratio $k_{NO}|_{CHAN} / k_{NO}|_{model}$ for Illinois#6, Pittsburgh # 8 and Knife River chars. Although all values are in the same order of magnitude as those of Chan et al (1983), the difference is as large as five fold for Knife River chars. The values for Illinois#6 chars were closer and those of Pittsburgh #8 in-between. Trying to explain the difference among chars of different coals, we may consider the carbon content of each char. Figure 4.21 presents the carbon content for the chars which k_{NO} was determined in Figure 4.20. It is clear that the lower the carbon content, the higher the discrepancy between Chan et al kinetics and the model predictions. Chan et al kinetics were determined for chars with carbon content of 80.5%, therefore it does not seem unreasonable that the char content (or conversely the ash content) may be responsible for the differences, with chars

with similar carbon content to the Chan char (Illinois #6) having similar kinetics.

Figure 4.20. Comparison between k_{NO} predicted by Chan et al (1983) kinetics and k_{NO} predicted by the model for different chars.

Figure 4.21. Carbon content for the chars used in the model. Data from Spinti (1997).

Figure 4.22 presents the relation between the NO reduction reaction constant (k_{NO}) as determined by the optimization routine, and the char carbon content. As it can be seen for Pittsburgh #8 and Illinois #6 chars there is a good correlation between these two variables. The higher the carbon content, the higher NO reduction constant. Even the slopes for Illinois #6 and Pittsburgh #8 lines are very similar. On the other hand, Knife River chars present a different behavior. The reason for this is unclear, although one can argue that at these very low carbon content values a different behavior may be expected and also that only with two points it is questionable to derive any trend.

It is interesting to note that Wang and Thomas (1996) found that higher rank coals (higher %C) had a higher NO_x production, also Shimizu et al found for combustion under fluidized bed conditions that higher carbon contents lead to higher conversions of char-N to NO_x. This may be in disagreement with the previous discussion. However Wang and Thomas (1996) explain their results on the basis of higher reactivity (measured as the temperature for 50% char consumption) of low rank coals and not on carbon content itself. Likewise, Shimizu et al (1992) found a correlation between surface area (not %C) and NO_x production.

Figure 4.22. Relation between NO reduction constant as predicted by the model and char carbon content.

A different way of representing the relation of Figure 4.22 is by plotting k_{NO} against char burnout. This is presented in Figure 4.23. Again there is a good correlation for Illinois #6 and Pittsburgh #8 chars. Higher burn-out represents lower NO reaction rate. This fact has already been reported by Guo and Hecker (1996) and Phong-Anant et al. In the first of these studies it is observed that the rate of NO_x reduction by char decreases by a factor of three as the carbon conversion increases from 0 to 80%. Phong-Anant et al (1985) have found that, during the combustion of chars at pulverized coal combustion conditions, the conversion of char-N to NO increases with burnout, which may be explained by a decrease on the NO reduction rate.

The reason for the different behavior of Knife River chars is again unclear, but the scarcity of data as well as the very high burnout level may be possible explanations.

Figure 4.23 Relation between NO reduction constant as predicted by the model and char burnout.

5.0 Experimental Studies of Heavy Metal Partitioning during Low NO_x Firing

5.1 Introduction

Particulate emissions from coal combustion have been a health and environmental concern since the beginning of the industrial revolution. Advances in boiler design and in post-combustion gas cleaning have greatly reduced the emissions from power plants but the fine particle emissions from combustion remain a concern. Recent studies (Schwartz and Dockery 1992; Dockery, Pope et al. 1993) indicate that current ambient air standards for fine particulate are still inadequate to protect the health of the most sensitive individuals. A goal of applied coal combustion research is increasing energy efficiency through advanced boiler technology while achieving emission control at reasonable cost. Better understanding of the interaction between combustion conditions and emissions is needed to allow quantitative evaluation of process alternatives.

Laboratory experiments and field studies during the past 20 years have shown that the fly ash from coal combustion has a bimodal size distribution. A large particle mode is formed by the coalescence of mineral inclusions in the char and a fine particle mode is formed by a vaporization and condensation mechanism (Damle, Ensor et al. 1982). The fine particles have a different bulk composition than the large particles and the structure is layered with the surface enriched in volatile elements (Neville and Sarofim 1982; Linak and Wendt 1994).

An extensive series of experimental studies, largely by Sarofim's group at MIT (Sarofim, Howard et al. 1977; Neville, Quann et al. 1981; Haynes, Neville et al. 1982; Neville and Sarofim 1982; Quann, Neville et al. 1982; Quann and Sarofim 1982; Kang, Helble et al. 1988; Helble and Sarofim 1989; Barta, Vámos et al. 1990; Barta, Toqan et al. 1992), lead to a general consensus of the fly ash formation mechanism. A large particle mode is formed from the residual ash from individual coal particles and the size distribution is determined by competition between coagulation and fragmentation mechanisms. The fine particles are formed from volatile species formed in the reducing zone near the char which then diffuse into the bulk gas, oxidize to form supersaturated vapor, homogeneously nucleate to form primary particles and heterogeneously condense to produce a submicron particles with a layered composition. The fine particle size distribution evolves as the primary particles collide and either coalesce or stick to form aggregates.

The existence of a bimodal size distribution was first predicted from aerosol dynamics models (Flagan and Friedlander 1976) and electrical aerosol analyzer measurements subsequently confirmed the submicron mode in utility boilers (Ensor, Cowen et al. 1979)(McElroy, Carr et al. 1982). Several studies using well-controlled laboratory furnaces to study fine particles from coal showed good agreement between model predictions and the experimental data (Flagan and Taylor 1981; Neville, Quann et al. 1981; Taylor and Flagan 1982; Helble and Sarofim 1989). Agreement of these models with field measurements on utility boilers was poor. The models predicted the shape of the distribution but the experimental data and model

predictions differed by one or two orders of magnitude in number concentration (Damle, Ensor et al. 1982). Explanations proposed in the literature included effects of coal composition, use of empirical factors for the vaporized ash fraction, site-dependent variability, and coagulation in the probe.

The modification of the furnace mixing and temperature pattern is now widely used as a NO_x control technique. The interaction between NO_x control and the size distribution and composition of the fine particle emissions is an unresolved question. Cato conducted the first extensive field study that compared the effects of combustion modifications on NO_x, particles, and burner efficiency (Cato, Hall et al. 1977). Taylor and Flagan (Taylor and Flagan 1982) summarized data from both laboratory furnaces and full scale power plants and concluded that the combustion modifications that reduced NO_x also reduced the submicron particulate. Linak (Linak 1985) reported not finding the correlation between NO_x and fine particles that was reported by Taylor and Flagan.

This experimental program was designed to provide additional data on the effect of in-furnace NO_x control techniques on the metal vaporization. The selected combustion conditions were determined by concurrent NO_x control experiments [discussed in previous sections].

5.2 Experimental Methods

The laboratory samples were produced in a 29 kW, down-fired, U-shaped furnace with an inside diameter of 0.16 m and an overall length of 7.3 m. Ports along the length of the furnace are available for injecting fuel or air and for extracting samples. The furnace has a Reynolds number, based on furnace diameter, of 1000-2000 depending on stoichiometric ratio and temperature. A high-volatile, bituminous-b Utah coal from the Wasatch Plateau field was pulverized to 70% less than 200 mesh. The coal heating value was 29 MJ/kg and the ASTM volatiles were 40% on a dry basis with 9% ash. The furnace, coal burners, gas analysis instruments, and coal analysis are described elsewhere. (Spinti 1997; Veranth 1998)

The test conditions are summarized in Table 5.1. The base case (abbreviated BASE) used a premixed burner in which the coal and combustion air passed through a water-cooled grid into the furnace. This simulates the rapid fuel and air mixing which occurs in older boiler designs. Two experimental conditions used this same premixed burner in conjunction with staged combustion. The coal devolatilization and the initial char oxidation took place at an overall stoichiometric ratio of 0.85, then burnout air was added which brought the stoichiometric ratio to 1.15. The staging air was added at ports which gave residence times in the reducing zone of approximately 0.5 second for condition STG@0.5S and 1.5 seconds for condition STG@1.5S respectively. The low-NO_x burner condition, abbreviated AXIAL, used a long axial flame produced by concentric injection of natural gas, coal plus primary air, stabilization natural gas, and secondary air, which created reducing conditions in the core of the flame. For condition REBURN an ammonia-spiked natural gas flame was used to simulate the combustion products of a low-NO_x coal burner. Pulverized coal followed by burnout air were injected downstream to create a short reducing zone. The stoichiometric ratio was calculated as the measured moles of

Table 5.1 Nominal Combustion Conditions Used in this Study.

Condition Description		BASE base case	STG@1.5S staging - long time	STG@0.5S staging - short time	AXIAL long axial flame	REBUR coal reburnin
Burner configuration		Premix	Premix	Premix	Diffusion	Premix
Thermal input, coal	KW	29.3	29.3	29.3	29.3	6.4
Thermal input, natural gas	KW	none	none	none	0.99	29.3
Distance to air staging port	m	a	3.17	1.36	a	a
Time to air staging port	s		1.5	0.5		
Distance to reburning port	m	a	a	a	a	2.89
Time to reburning fuel port	s					1.1
Distance to burnout air port	m	a	a	a	a	3.73
Time to burnout air port	s					1.4
Distance to exit sampling port	m	6.17	6.17	6.17	6.17	6.17
Time to exit sampling port	s	2.78	3.12	2.90	2.82	2.35
Target reducing zone S.R. ^b		a	0.85	0.85	variable	0.85
Target exit S.R. ^b		1.15	1.15	1.15	1.15	1.15
Exit oxygen concentration	%	2.87±0.41	2.89±0.38	2.78±0.15	3.15±0.5	2.78±0.1
Exit NO _x concentration	ppm	947±32	171±17	465±29	456±56	242±7
Number of runs for gas composition		14	17	16	8	6
Temperature 2 m from burner	K	1382±17	1322±4	1355±26	1389±9	1382±3
Temperature at exit port	K	855±19	818±7	845±12	803±16	902±23

a. n/a: not applicable

b. S.R.: Stoichiometric Ratio

c. Measured data are the mean ± standard deviation for the available furnace sampling runs.

oxygen supplied divided by the calculated oxygen for complete combustion based on the coal analysis.

The exit temperature and oxygen and NO_x (sum of nitrogen oxide and nitrogen dioxide) concentrations were continuously logged during the experiments. The furnace temperature was measured using a ceramic-sheathed type B thermocouple which was able to operate for extended periods, even with the high ash loading produced in the core of a pulverized coal flame. A previous study documented the difference between the type B thermocouple reading and suction pyrometer readings.(Spinti 1997)

A water-cooled probe was used to collect the furnace gas and particles. Preliminary experiments indicated that the selected procedures produced acceptable samples of the particles smaller than 10 μm aerodynamic diameter.(Veranth 1998) Larger particles settle along the horizontal portion of the furnace and cannot be collected quantitatively. Rapid dilution at the probe tip was not used since the transport time inside the probe was small compared to the time from the burner to the sampling port.

An Andersen 8-stage 1-acfm cascade impactor and preseparator were used with methods that were originally developed to produce large samples of oil-free particles for toxicology studies (Smith and Aust 1997). A fraction enriched in particles larger than 10 μm aerodynamic diameter was collected in the preseparator. The deposits collected on impactor stages 1, 2 and 3 were combined to make a sample enriched in particles between 2.5 and 10 μm . Stage 5 produced a sample enriched in particles between 1 and 2.5 μm . Stage 7 plus the final filter were combined to produce a sample of submicron particles. Oiled substrates were used on impactor stages 1, 4, and 6 to provide a separation. Figure 5.1 illustrates the sampling apparatus.

Duplicate furnace samples were collected for metals analysis at each combustion condition. Additional samples were collected at each combustion condition to determine fly ash mass distribution and carbon content.

The particle samples for metals analysis were washed from the collection substrates and stored in clean glass containers. An outside laboratory (Chemical and Mineralogical Services, Salt Lake City) was used for the metals analysis. The particle samples were washed from the storage containers into teflon beakers for acid digestion. The digestion was done using a hot mixture of hydrochloric, hydrofluoric, nitric, and perchloric acid. The resulting solution of metal salts was evaporated to near dryness then redissolved in distilled water and hydrochloric acid. The samples were analyzed for the major elements (Si, Al, Ca, Mg, Na, K, and Fe), for the first row transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn), and for three listed toxic metals (Sb, As, Pb). The elemental composition was determined using Perkin Elmer ICP/MS (ion coupled plasma / mass spectroscopy) equipment. Sodium and potassium were analyzed by FEAA (flame emission atomic absorption) and iron was analyzed by both ICP/MS and FEAA. Samples of NIST 1633b - Standard Reference Material for Constituent Elements in Coal Fly Ash were run along with the laboratory-generated fly ash samples for the various combustion conditions. Blanks were run to determine background levels of metals due to laboratory contamination and due to impurities in reagents.

Figure 5.1 Particle measurement equipment schematic.

Analytical results were reported as the weigh fraction of each element in the sample. This raw data was converted to mass of metal on both a total ash and on a carbon-free basis in each fly ash size fraction per mass of coal burned.

5.3 Results

Axial profiles of furnace temperature NO_x is shown for the various combustion conditions in Figure 5.2. Staging and coal reburning resulted in substantial reductions in exit NO_x compared to the base case. The difference in the measured temperature distribution along the length of the furnace between conditions was less than the change calculated from material and energy balances due to the transient heat transfer between the laboratory furnace wall and the combustion gas. Each coal combustion experiment lasted 4 - 6 hours with the furnace temperature being maintained between experiments using natural gas. The time for the furnace wall temperature to reach steady state at a new combustion condition is 2 - 3 days.

The metals analysis showed the expected enrichment of previously-reported volatile elements, such as sodium, potassium, iron, zinc, antimony and lead, in the finest flyash size fraction. As required by mass balance, less volatile elements such as aluminum were depleted in fine particles. Most of the coal fly ash consists of particles larger than about 5 μm with only a few percent of the mass being in the submicron range. Because of this size distribution, only a small mass of the PM1-enriched fraction was collected before the upper stages of the Andersen

Figure 5.2 Stoichiometric ratio and NO_x concentration versus distance.

impactor became overloaded. For the PM₁-enriched fraction, the concentrations of many elements was near the limit of detection. Also, for many metals there was poor agreement between the duplicates taken at the same combustion condition. Because of these experimental limitations there were no clear trends indicating differences in metals vaporization between the five combustion conditions.

6.0 Conclusions

This program encompassed a number of studies surrounding issues related to NO_x formation and control, and furnace operation under such low NO_x conditions. The following sections summarize salient conclusions from these studies.

6.1 Conclusions - NO_x Formation from an All-Axial Multi-Fuel Burner

An understanding of the effect of near burner aerodynamics on NO formation is essential in achieving the ultra low NO levels mandated by the new U. S. Clean Air Act Amendments for a hot-walled furnace utilizing a naturally staged, gas stabilized burner. Pilot-scale experiments were carried out under these conditions and the results of these experiments indicate that:

1. Small amounts of natural gas can be used to enhance the stabilization of axial pulverized coal flames and to reduce their NO emissions.
2. Primary jet velocity is the critical contributor to near burner NO production in these gas stabilized axial flames. A doubling in jet velocity causes NO levels to double.
3. NO emissions are not significantly affected by the use of a vitiated secondary oxidant (which is desirable for combined cycle efficiency in some modern power generation systems).
4. Ultra low NO levels (below 90 ppm) can be achieved without the use of SCR or SNCR by optimizing burner performance in conjunction with staged combustion and reburning.

Near burner aerodynamics, however, only affect the fate of nitrogen contained in the volatiles (volatile-N). Nitrogen contained in char (char-N) reacts on a much longer time scale than volatile-N. Hence, although the use of gas stabilization and low primary jet velocities reduces NO_x formation in the near burner region, the affect of such combustion modification techniques on the fate of char-N required additional research as described below. What is clear is that at the low NO levels achieved in these experiments with the all-axial multifuel burner, an understanding of fate of all the nitrogen contained in the coal is necessary if any further reductions in NO_x formation are to be achieved.

6.2 Conclusions-Important Features of this Char-N Data Set

There are several unique features of the char-N experimental data presented in this report. First, the coal chars used in the study were prepared and burned at pc conditions, so all results are specifically applicable to such conditions. Second, the experiments were conducted with a premixed burner, thus eliminating many of the mixing effects which would add another degree of complexity to the data analysis. Third, gas phase NO_x measurements were made with two different instruments- a chemiluminescent NO_x analyzer and an FT-IR. Hence, all results can be

double checked using readings from both instruments. Fourth, the scale of the experiments is much different than that of most other experiments related to the fate of char-N. The present experiments were conducted in a laboratory reactor with a nominal firing rate of 29.3 kW; other researchers have used small fluidized beds which simulate single particle combustion, drop tube furnaces, and thermogravimetric analyzers. Thus, the mechanisms postulated by other researchers based on the more fundamental scale of their experiments can be tested against the present data, which was obtained at a much larger scale.

In addition to being unique, the char-N data collected and analyzed in this report fulfilled the experimental objectives outlined in Section 3.1. The first objective was to isolate char-N from volatile-N in order to study char-N. The isolation of char-N was achieved by collecting partially burned coal (i.e., char) from the U furnace and then burning that char in subsequent experiments. The second objective was to collect all data at pc conditions so that results were relevant to pc combustors. This objective was met by collecting chars from coals which were partially burned at pc conditions and by burning all chars as simulated coals in the U furnace at pc conditions. The third objective was to determine the effects of various combustion parameters including O₂ concentration, furnace temperature, NO_x concentration, and parent coal of the char on NO_x formation from char-N. The effects of all these parameters were tested and the results were plotted and analyzed in this report. The fourth objective was to obtain a reliable data set for char-N model development and validation. To fulfill this objective, the repeatability of the data was checked by repeating various tests and by comparing NO_x results obtained from both the chemiluminescent NO_x analyzer and the FT-IR. Also, furnace baseline conditions were checked at least daily. The fifth and final objective was to identify current char-N models which might explain observed experimental results and outline modifications needed to these models or propose new models which could be used to explain experimental data. This objective was fulfilled in Section 4.0, where predicted results from different models were compared to the experimental data. Clearly, all five experimental objectives were met.

6.3 Conclusions-Mechanistic Insights

The present char-N data also provide new mechanistic insights into the fate of char-N. To begin, interactions between NO_x formed from volatile-N and NO_x (or NO_x precursors) formed from char-N are extremely important. The amount of NO_x present in the gas phase when the char began to burn (i.e., initial NO_x) had a greater effect on char-N to NO_x conversion than any other parameter tested. In all initial NO_x experiments, conversion decreased sharply with increasing initial NO_x concentration, an indication that the conversions of char-N to NO_x for all chars in the test suite follow the same mechanistic routes.

Next, the reduction of NO on carbon in the char does not appear to be the most significant source of NO_x reduction during char oxidation. The low levels of char-N to NO_x conversion observed at high initial NO_x concentrations can only be accounted for by assuming that two other sources of NO_x reduction are also occurring: the reaction of NO with char-N to form N₂O and subsequently N₂ and the release of char-N as HCN (or some other NO_x precursor) followed by the homogeneous reactions of HCN to form NO and N₂. The homogeneous N₂ pathway is at least as important as the heterogeneous reduction pathways.

Additionally, O₂ concentration has the same effect on char-N to NO_x conversion as it does on volatile-N to NO_x conversion; as O₂ concentration increases, char-N conversion to NO_x also increases. This observation holds true at all levels of initial NO_x tested (0-900 ppm) and indicates that even as initial NO_x concentration changes, the same char-N oxidation mechanisms are occurring. This observation also reveals that char-N oxidation to NO (either heterogeneous or homogeneous) must outpace the rate of NO_x reduction to N₂ as O₂ concentration increases.

Lastly, the rate of char-N (or HCN) oxidation decreases more rapidly with temperature than the rate of heterogeneous NO_x reduction or direct N₂ formation via HCN. This conclusion is the result of experimental data which show that conversions of char-N to NO_x at all initial NO_x levels except 0 ppm are lower at lower furnace temperatures. Conclusions about what is occurring at 0 ppm initial NO_x are difficult to draw for two reasons. One, the data are ambiguous. Two, both homogeneous and heterogeneous N₂ formation mechanisms require NO as a reactant and, since there is no NO present at first, analysis becomes more complicated.

Further analysis of the char-N experimental data yields other information about the fate of char-N. First, the data collected at various initial NO_x levels suggest a lower limit to the minimum achievable NO_x levels from char-N because char-N to NO_x conversion decreases at the expense of increasing conversion of volatile-N to NO_x (i.e., initial NO_x). Even if NO_x formation from volatile-N could be reduced to 0 ppm, data from simulated coal experiments in artificial oxidant indicate that char-N to NO_x conversion would still be on the order of 40-60%. Second, the accurate prediction of NO_x formation from char-N depends on the accurate modeling of the nitrogen partitioning between volatile-N and char-N. This conclusion is based on data from experiments with a series of Illinois #6 coal chars of varying nitrogen content where char-N to NO_x conversion increased with increasing nitrogen content of the char.

6.4 Conclusions - Modeling Studies

An analytical solution of a simple single particle model for the char-N conversion to NO was developed. This model was in agreement to Visona and Stanmore's previous model (1996) and with general experimental observations.

Model predictions were compared to Spinti's (1997) results for the combustion of char in a furnace at PC conditions. The model predicted in a satisfactory way the char-N conversion to NO at low NO bulk concentration. However at high NO bulk concentration, the model underpredicts char-N conversion to NO. Additional research will be needed to resolve these discrepancies.

The value of the rate constant for NO reduction on char surface determined by the model is similar to kinetics obtained by Chan et. al (1983) for chars with carbon content comparable to those in the chars used in the experiments by Chan et. al. The higher the difference in carbon content between modeled chars and the Chan et. al (1983) chars, the higher the discrepancy in the rate constant. In the same way, there is good correlation between the amount of carbon content and the rate constant for NO reduction on char surface. Higher carbon content implies higher rate constant. Or in an alternative way, higher burnout implies lower reduction rate.

In conclusion, the model with the fitted NO reduction kinetics can be used in CFD codes for NO prediction. The present results suggest that the value of K_{NO} is a function of NO conversion and this variation can be built into the model. Additional data will be needed to better establish the functionality and the mechanism for the changing coefficient with conversion.

6.5 Conclusions - Toxic Metal Behavior under Low NO_x Conditions

These experiments indicated that any differences in metals vaporization between the five combustion conditions tested were small. The use of staged combustion, long axial flames, and coal reburning for in-furnace NO_x reduction is not contraindicated by associated substantial increases in the emissions of toxic metals. Detection of any differences between the metals content of the PM_{2.5}- and PM₁-enriched fly ash produced from these laboratory combustions conditions would require both improved particle collection and analysis methods. Also, due to the variation between duplicates, a much larger number of furnace samples would need to be collected and statistical analysis of results would need to be needed to separate random error from real differences in metal partitioning.

6.6 Suggestions for Future Work

Although the present work produced new insights into the fate of char-N, much work is left to do in three different areas: fundamental mechanisms, additional data collection at realistic pc conditions, and improved modeling of both the fate of char-N and nitrogen partitioning between volatile-N and char-N. Possible directions to be taken in each of these three areas are given below.

In terms of fundamental mechanisms, the char-N data from the present experiments cannot be used to definitively say the route to NO_x formation from char-N is primarily homogeneous, heterogeneous, or a combination of the two. Much more fundamental, single particle-type experiments must be conducted. Recent work by Winter et al. (1996) in which homogeneous reactions of nitrogen-containing compounds from the char-N are frozen is a step in this direction and should be continued. Another possibility for settling the heterogeneous versus homogeneous question lies in the realm of theoretical chemistry. Fundamental ab initio calculations, which refer to the solution of the Schrödinger equation in quantum theory, could be performed on the char molecule to determine which species were being evolved in an oxidative environment. There is a drive in theoretical chemistry today to do ab initio studies of larger and larger molecules, and large biological molecules have already been subjected to such studies. Hence, it does not seem unreasonable to suggest that within the next few years, ab initio studies on molecules as large as a char particle (or at least a portion of one) could be performed.

Additional char-N data collection at realistic pc conditions is also needed. To begin, chars from a larger variety of parent coals should be tested to confirm the trends seen in the present experiments. Next, chars in both the early and late stages of char oxidation should be collected and then burned as simulated coals in order to determine the effect of the degree of char oxidation on char-N to NO_x conversion. Finally, the importance of NO reduction on carbon in

the char needs further evaluation. This evaluation could be done in two ways. One, Nuchar (or some other carbon-based material with a very low nitrogen content) could be burned like the parent coals at pc conditions and collected after partial oxidation had occurred. This partially-oxidized Nuchar, which would thus have undergone the same preparation process as the coal chars, could then be used in simulated coal experiments to study NO reduction on carbon. Two, simulated coal experiments could be performed on a high carbon, very low nitrogen char with a surface area similar to that of the coal chars.

From a Char-N model development perspective, additional data will be needed to better establish the functionality and the mechanism for the changing kinetic rate coefficient with conversion and the effects of initial NO concentration on the overall rate. Although the proposed model is capable of predicting the effect of initial NO on the overall NO reduction rate at lower levels of initial NO, there are some discrepancies at high levels of initial NO.

7.0 References

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A. Appendix A - Experimental Apparatus

All equipment used in the University of Utah experiments will be described in detail in this appendix. Detailed information will be provided on the physical facilities (combustor, burner, etc.) as well as instrumentation, sampling systems, and temperature measurement.

A.1 U Furnace

A new bench scale test facility was designed and built at the University of Utah for the experiments described in this thesis. This new multifuel combustion research facility, shown in Figure A.1, has a U configuration and is down-fired; it will hereafter be referred to as the U furnace. Its nominal firing rate is 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 as described in Section A.1.4.

A.1.1 Design of the U Furnace

The U furnace is made up of seven sections. Each section will be discussed in detail in the following paragraphs. All sections were fabricated from carbon steel unless otherwise indicated on the design drawing.

The burner is mounted to the top of Section 1. Section 1 also has a large, water-cooled window port for viewing the flame (quartz glass is used for the window), three 5.25 cm diameter ducts located at the same level as the top of the window, and two sets of opposing ports located below the window. Although the window was important for flame observation, radiant heat losses to the window were large. Consequently, a refractory plug was inserted into the window opening and remained there for all char-N experiments. The three ducts are used for flame ignition and detection. A pilot burner is located in one of the two opposing ducts. A UV flame detector (also called a “peeper”) is located at the end of the duct that directly opposes the duct containing the pilot burner. The third duct, located at 90° to the other two, also has a peeper located at its end. The pilot burner is used to ignite the main burner, and the peepers detect UV radiation from the flame once it is ignited. The two sets of opposing ports are used for inserting sample probes, thermocouples, etc. into the combustion chamber. Sampling ports are numbered by section in the direction of gas flow. In addition, the designations N, S, E, and W are included to indicate on which side of the furnace the port is located. Hence, the opposing ports just below the level of the window are ports 1-1N and 1-1S, and the opposing ports at the very bottom of Section 1 are ports 1-2N and 1-2S. This numbering system will be used subsequently to describe where sample probes and thermocouples were inserted.

Section 2 has three sets of opposing sampling ports, numbered in order according to the direction of gas flow as ports 2-1E and 2-1W, ports 2-2E and 2-2W, and ports 2-3E and 2-3W. There are no other special features of Section 2. Furnace flow changes direction by

Figure A.1 . Multifuel combustion research facility

90° in Section 3; furnace flow is vertical entering the section and horizontal leaving it. This sudden change in flow direction required special design considerations for the burning of solid fuels because larger particles would have enough momentum to deposit in the corner. In order to avoid a buildup of particles that could potentially plug the furnace and be difficult to clean out, a removable drawer was designed into Section 3. This drawer, known as the ash drawer, is lined with both refractory and insulation board. It sits directly below the combustion chamber, so any solids that aren't carried around the corner with the flow are deposited in this drawer. The drawer is removed from the furnace at frequent intervals and any collected solids are disposed of. Section 3 also has one set of opposing sampling ports (ports 3-1E and 3-1W) and a window port. The window consists of a threaded pipe welded onto a plate that is bolted onto the window port's flange. A screw cap with quartz glass recessed in the cap is then screwed onto the threaded pipe. The window diameter is approximately 5 cm.

Section 4, positioned horizontally, has four sets of opposing sampling ports. It has no other special features. Section 5 is similar to Section 3 in that the furnace flow changes direction again- from horizontal to vertical. Section 5 has one window port that is exactly the same as the one described on Section 3. Section 5 has no sampling ports or ash drawer. When solids do build up in the corner, cleaning is done through the window port.

Section 6 is the longest of all the sections. It has four sets of opposing sampling ports (east and west sides), again numbered in order in the direction of gas flow. There are also ports located at the top and the bottom of Section 6 (north and south sides) as well as two circular ducts. These additional ports at the top and bottom were originally for use by auxiliary burners with the circular ducts used for flame detection by peepers. However, the auxiliary burners were not required for these tests, so solid plates were bolted onto these four openings and the ducts were capped.

The last section, Section 7, has one window port located on top and no sampling ports. The window is much larger than either the Section 3 or 5 windows. It consists of a 18 cm by 7.5 cm rectangle of quartz glass recessed in a metal box that is bolted to the flange on the window port. The furnace flow again changes direction by 90° as it exhausts through the rear of Section 7. Upon exiting the furnace, the flue gas enters a series of insulated, flanged elbows and tees that redirect the flow up and over the furnace. The flue gas then enters a long section of bare pipe where significant heat loss occurs; this section ends in a tee. Two air-atomized water spray nozzles are mounted to one leg of the tee to cool the flue gas as it travels down the long pipe. The cooled flue gas then enters a flue duct in the laboratory that is maintained at a negative pressure by an evacuation fan on the roof of the building. By exhausting the furnace flue gas into this duct, the furnace can be maintained at slightly sub atmospheric pressures at all times.

A stand was fabricated for the furnace in order to distribute the weight of the furnace as evenly as possible over the I-beams in the floor of the laboratory. The stand was constructed from 10 cm I-beams and is sketched in Figure A.1. Angle iron welded to the shell of the U furnace in eight locations is bolted to four of the I-beams running crosswise.

With this design, the U furnace is completely suspended above the stand except where it is bolted with the angle iron.

A.1.2 Piping and Flow Metering

The furnace is equipped with piping for various natural gas and air streams including pilot burner air and gas lines, a main combustion air line from which a primary air line and a secondary air line tee off, a main burner gas line, and additional lines that were employed for various purposes during the experiments. Two electrically-heated tube heaters mounted in series are located in the secondary air line. These heaters are used to heat the secondary air prior to its entering the burner.

All air and natural gas flows into the furnace are metered using rotameters equipped with valves and pressure gauges. Actual flow rate is determined by the position of the float in the rotameter, the specific gravity of the fluid flowing through the rotameter (most rotameters are calibrated for air), and the pressure of the fluid in the rotameter according to the equation

$$Q_2 = Q_1 \sqrt{\frac{P_2 \times 1}{P_1 \times SG}} \quad (1)$$

where

Q_1 = Observed flowmeter reading

Q_2 = Actual flow corrected for pressure and specific gravity

P_1 = Atmospheric pressure at sea level

P_2 = Actual pressure inside flowmeter (local atmospheric pressure + pressure inside flowmeter)

1 = Specific gravity of air

SG = Specific gravity of gas being used in flowmeter originally calibrated for air.

All flows except the main combustion air flow are metered using Dwyer rotameters. The pilot air and gas flows use Dwyer Series RMB rotameters which have a guaranteed accuracy of +/- 3% of full scale. All other air and natural gas flows (except main combustion air) are metered with Dwyer Series RMC rotameters which are accurate to +/- 2% of full scale (Dwyer, 1993). The main combustion air is metered with a Brooks Model No. 1110-09K3G1A rotameter which, according to product literature, is accurate to +/-2% of full scale. Calibration data for the Brooks rotameter can be found in Appendix A.

The main combustion air line tees off to provide air to both the primary and secondary air lines. There are no flow constrictions in the secondary air line from the tee to the burner. The flow constrictions in the primary air line are a rotameter (Dwyer Series RMC) and a valve located just downstream of the tee. Flow rate in the secondary air line is determined by subtracting the flow rate through the primary air rotameter from the flow rate of main combustion air through the Brooks rotameter.

A.1.3 Water cooling

Water cooling is used at several furnace locations. First, the premixed burner requires water flow through its radiation shield, as described in Section B. Next, water flows through copper coils braised on to various Section 1 locations including the top plate and the area immediately surrounding all three circular ducts. Copper coils were also braised on to the shell around the windows in Sections 3, 5, and 7, but it was not necessary to flow water through these coils. Finally, water flows through stainless steel tubing that is wound around the tee located at the exit of Section 7.

A.1.4 Refractory

As mentioned previously, the walls of the U furnace are a composite of castable refractory and insulation board. The materials in the composite wall were obtained from the A. P. Green Company. Table A.1 lists those materials along with some of their properties. Figure A.2 and Figure A.3 show how the refractory and insulation board are layered in each section of the U furnace.

Table A.1 . Insulating materials used in the U furnace.

Name of Material	Type of Material	Density (kg/m ³)	Mean Temp. (K)	Approx. k Values (W/m ² /K/cm thickness)
Greencast-94 Plus	Castable refractory	2561	700	29.49
			955	26.58
			1145	24.57
			1365	23.90
			1590	24.13
Kast-o-lite 30 Plus	Castable refractory	n/a	700	6.48
			955	6.90
			1145	7.33

Figure A.2 . Front view of refractory layers in U furnace.

Figure A.3 . Side view of refractory layers in U furnace.

Table A.1 . Insulating materials used in the U furnace.

Name of Material	Type of Material	Density (kg/m ³)	Mean Temp. (K)	Approx. k Values (W/m ² /K/cm thickness)
Insboard 2300	Insulation board	28.8	1365	7.73
			1055	2.02
			1205	2.36
Insblok-19	Insulation board	30.7	640	1.41
			730	1.67
			790	1.86

Heat transfer calculations by the A. P. Green Company were used to estimate the temperature drop across the composite layer and to approximate the surface temperature of the furnace shell. Safety considerations required that the shell temperature not exceed 420 K. Performing the calculations with the composite layer in Section 1 and with a hot face temperature of 2035 K, the temperature drops across the different layers are as follows: Greencast 94 Plus layer = 228 K, Kast-o-lite 30 Plus layer = 462 K, Insboard 2300 layer = 271 K, and Insblok-19 layer = 683 K. These temperature drops yield an estimated shell temperature of 389 K. Actual shell temperatures measured after the furnace had been fired continuously for a period of several weeks indicate that Section 1 shell temperatures do reach 410 K in some locations.

Each section of the U furnace was poured separately. The refractory was firmly fixed to the steel shell of the furnace by steel anchors which were welded to the shell. The anchors extended into the innermost layer of refractory and were located on 15 cm centers. In Sections 1, 2, and 3, wooden forms were used to shape the outermost refractory layer (Kast-o-lite 30 Plus). With the exception of the horizontal component of Section 3, the innermost refractory layer (Greencast 94 Plus) was poured around a PVC pipe with an outside diameter of 15.9 cm. For all horizontal sections of the furnace, the innermost refractory layer was poured around a wooden form with a cross sectional area of 17.8 cm x 17.8 cm. In Sections 6, 7, and the vertical component of Section 5, the innermost refractory layer (Kast-o-lite 30 Plus) was poured around the 15.9 cm PVC pipe. The channels cast in the refractory layer of Section 6 (see Figure A.2) were formed by pouring refractory around channel forms made from foam core board. These channels, whose original purpose was to provide auxiliary heating in Section 6, were not required for this program. The 5.1 cm diameter ducts in Sections 1 and 6 were formed using PVC pipe as the mold. Wooden forms were used in all other locations where refractory shaping was required.

A.1.5 Furnace Electronics and Safety System

The electronics section of the main control panel by the U furnace is diagrammed in Figure A.4. Other portions of the panel contain rotameters, pressure gauges, regulators, etc. The “Main” button, when pulled out, turns on power to the furnace electronics. Power to each subsystem is controlled by its respective push/pull button. Once power to a subsystem has been turned on, the on/off push button switches can be used. For example, in order to turn on the coal/char feeder, the Coal Feeder System push/pull button must be pulled out and then the Coal Feeder on/off push button switch must be pushed on. At this point, a switch on the feeder can be flipped on and the augers will begin to feed coal. There is some redundancy in this system, but this redundancy ensures that the operator thinks through the process before turning anything on.

The selector switches have several purposes. When the Electric Heater Safety Bypass switch is set to the off position, the electric heaters can be turned on even if there is little or no secondary air flow. This feature permits the electric heaters to be serviced periodically. The Pilot Sparker switch allows the sparker to be used to light more than one pilot burner. Since only the main pilot burner was used in the char-N tests, the switch was set on that burner and never moved.

The U furnace is designed to be run continuously in a safe operating mode. Four safety parameters are constantly monitored: air supply pressure, water supply pressure, flue (evacuation) duct vacuum pressure, and flue duct temperature. An out-of-range reading for any one of these parameters indicates a dangerous operating condition. When an out-of-range reading occurs, solenoid valves, installed in all natural gas lines between the gas supply line and the combustor, are closed. Also, the electric heaters mounted in the secondary air line are shut off as is the coal/char feeder. Out-of-range readings do not cause the air supply to the combustor to be shut off unless the cause of the shutdown is lack of air supply pressure. In addition to these four parameters, the flame is continuously monitored by three peepers installed in parallel. If none of the peepers picks up a sufficient UV signal, the natural gas solenoid valves are closed.

There are several additional safety features. First, a pressure switch in the secondary air line monitors pressure in that line downstream of the rotameter. If the pressure drops too low, the electric heaters are shut off. This switch was added in the event that the secondary air is turned down too low (or even turned off) because the electric heaters can easily be damaged with little or no air flow through them. Second, there are two “Main” buttons installed, one on the main panel by the U furnace and the other in the control room. Both these buttons serve the same function. When punched in, all furnace systems are immediately shut down including the natural gas solenoid valves, the electric heaters, and the coal/char feeder. Thus, an operator can rapidly shut down the entire system without leaving the control room.

The three on/off push button switches that control the opening and closing of the natural gas solenoid valves (Main Pilot, Reburning Gas, and Main Gas) can only be turned on if two conditions are met. One, as mentioned above, the appropriate subsystem push/

Figure A.4. Electronic section of U furnace main control panel.

pull button must be pulled out. Two, the peepers must be able to detect a UV signal from the flame. The sparker is needed to light the pilot since the Main Pilot solenoid will not open and allow natural gas to flow until the peepers “see” a flame. A peeper located in the duct that directly opposes the pilot burner duct “sees” the spark produced by the spark plug and detects a flame. The Main Pilot solenoid can then be opened, and gas flows to the pilot burner where pilot air is already flowing. The spark ignites the fuel/air mixture and the peepers pick up this pilot flame. At this point, assuming main combustion air is already flowing, the Main Gas solenoid can be opened. The pilot flame, located directly beneath the main burner quarl, then ignites the main burner.

The Supplemental O₂ solenoid (controlled by an on/off push button switch) is used for experiments where a stream of pure O₂ needs to be fed into the main combustion air line. O₂ injection will be discussed in more detail later in this appendix. This solenoid cannot be opened unless there is sufficient flow in the main combustion air line. A pressure switch located in the main combustion air line will shut the solenoid if the pressure drops too low. This safety feature ensures that O₂ concentration in the main combustion air line is never high enough to be concerned about O₂ explosions.

A.1.6 Coal/Char Feeding System

All coals and chars tested in this thesis were fed using the coal/char feeding system sketched in Figure A.5. The major components of this system include a Ktron Model T20 Twin Screw Volumetric feeder, a pressure equilibration regulator, two sizes of eductors, and a primary air stream. Coal or char in the hopper is fed into the twin screws. The solid moves down the screws until it drops off the end of the screws into a short stainless steel coupling. A small line exits the cap on the top side of the coupling. This line is connected to both a Magnehelic (a pressure and vacuum gauge) and one side of a pressure equilibration regulator. A Teflon bellows is attached to the bottom edge of the coupling. The solid falls through the bellows and into a funnel which narrows to the inlet diameter of the eductor. Primary air being fed through the eductor picks up the solid and carries it to the burner. The pressure equilibration regulator is used to balance primary air pressure upstream and downstream of the nozzle in the eductor. In order to prevent solids buildup in the eductor inlet, a slight vacuum, measured by the Magnehelic, is maintained on the downstream side of the eductor nozzle. Two sizes of eductors are needed because high moisture coals tend to cake up in the inlet of the smaller eductor, necessitating the use of the larger eductor. Details about the calibration of the Ktron feeder are found in Appendix A of Spinti (1997).

A.2 Premixed Burner

The burner used for all experiments described in this thesis is a premixed burner that was specially designed and built for the present work. Figure A.6 is an assembly drawing of the burner. The burner is fabricated from all stainless steel parts.

Figure A.5 . Coal/char feeding system.

Figure A.6 . Assembly drawing of premixed burner.

A.2.1 Premixed Burner Design

The burner consists of five main sections. The first section includes inlets for the secondary air and the primary air/coal mixture and a mixing plate. This mixing plate is designed to produce a well mixed coal/air mixture in the second section, known as the mixing chamber. The primary air/ coal inlet pipe is welded to the mixing plate. The air/ coal mixture entering the burner is forced through six-3.6 mm holes equally spaced around a 0.86 cm circle on the mixing plate and drilled at an angle of -20° off the vertical. The secondary air enters the burner through two inlets and is forced through six-6.9 mm holes equally spaced around a 5.3 cm circle on the same mixing plate and drilled at an angle of $+15^\circ$ off the vertical. The two streams (primary/coal and secondary) impinge on each other approximately 2.5 cm below the mixing plate. Based on a typical run where primary air makes up 15% of the total combustion air, primary jet velocity exiting the holes is 22.8 m/s and secondary jet velocity is 35.4 m/s.

The second section of the burner, the mixing chamber, is where the two impinging streams are allowed to fully mix before entering the third section of the burner, the radiation shield. The purpose of the radiation shield is to prevent premature ignition of the fuel/oxidant mixture in the premixing chamber. The radiation shield consists of three rows of staggered stainless steel tubes (OD = 0.64 cm) that extend across the burner cross section. The staggered configuration prevents any direct line of sight from the combustor up into the mixing chamber. Water runs continuously from a manifold-type configuration through the bank of tubes. The estimated velocity of the fuel + air mixture through the radiation shield, assuming the combustion air is preheated to 530 K and the natural gas firing rate is 29.3 kW, is 12.0 m/s.

A water recirculation system was devised for the radiation shield in the event of an unexpected loss of supply water. If supply water pressure drops to zero, the pressure switch that monitors supply water pressure as part of the U furnace safety system will trip. This tripping will open two solenoid valves and close two others in the water lines feeding the radiation shield. The net effect is that water from a tank located above the furnace will be recirculated through the radiation shield, thus preventing any damage to the shield from furnace radiation.

Natural gas injection occurs just below the radiation shield in the fourth section of the burner. Natural gas enters the burner through two-1.3 cm OD tubes into an annular ring. The gas is then forced through eighteen-2.4 mm holes equally spaced around the diameter of the inner ring of the annulus into the flow of fuel + air coming through the radiation shield.

Turbulent jet mixing calculations were performed to determine the extent of mixing of the radially-injected natural gas with the flow of air from the radiation shield. Based on a natural gas firing rate of 29.3 kW with combustion air temperature decreased to 480 K due to the cooling effect of the radiation shield, calculations yielded the following information. At an axial location 0.64 cm below the gas injection point, the natural gas jets extend 4.6 cm radially into the air flow. At an axial location 1.3 cm below the gas injection point, the

jets extend 5.8 cm radially into the air flow. Since the inside diameter of the burner is only 6.3 cm, these calculations indicate that the natural gas is completely mixed across diameter of the burner only 1.3 cm below the point of injection.

The fifth and final burner section is refractory-lined with Greencast-94 Plus as shown in Figure A.6. The refractory layer is 3.3 cm thick. This section also has two 1.3 cm ducts that extend horizontally from the threaded pipe through the refractory layer to the burner interior. Peepers are mounted to the threaded pipe with a direct line of sight to the burner interior in case ignition occurs at this location and not down below the quarl where the other peepers are located.

A quarl, although not shown in Figure A.6, 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 (15.9 cm) over a length of 20.3 cm.

A.2.2 Premixed Burner Testing

The mixing capabilities of the premixed burner were tested with a variety of fuels by inserting a water-cooled gas probe into port 1-1N of the U furnace. The probe was moved to various radial locations and gas phase species concentrations were measured. For details on the sampling system used, Sampling System on page 149.

The radial NO and O₂ profiles obtained from these tests are plotted in Figure A.7 for four different fuels: natural gas, natural gas and char, Pittsburgh #8 coal, and Illinois #6 coal. Position 3 on the plot represents centerline and position 0 represents the wall. Data were logged every second for 3 min; each data point represents a 3-min average. Based on the both the NO and O₂ plots for all four fuels, radial variations in concentration appear to be small, indicating that the flame is well-mixed for all fuels.

More extensive testing of the degree of mixing achieved by the premixed burner was conducted using a Utah bituminous coal as the fuel. Two probes were used in these tests, a water-cooled probe and a quartz tube probe. Both probes have 90° bends at the tip. With this configuration, the probe tip can be located in line with the furnace flow at any radial location. Probe diameter was determined by 1) the desire to minimize flow field disturbances caused by the probe and 2) the need to have a big enough opening in the probe that it didn't constantly clog. The water-cooled probe had an OD of 1.9 cm and an ID of 6 mm. The quartz probe, made from a single piece of quartz tubing, had an OD of 6 mm and an ID of 4 mm. Both probes were long enough to sample 2.5 cm past the centerline of the furnace. The sample line consisted of a two fiberglass filters, a stainless steel water trap inside a refrigerator, and Teflon lines.

The probes were inserted at three different furnace locations: port 1-1 (N and S), port 3-1 (E and W), and port 4-4 (E and W). Sampling was done at both east (or north) and west (or south) ports of each location to remove any sampling bias. Also, the sample probe tip was placed at different radial locations in a random order. Data were logged every five

seconds for 100-250 seconds with the majority of the points logged for 140 seconds. Data near the burner were difficult to obtain with the quartz probe because of its fragility. The tip broke off several times, which meant the whole probe had to be replaced.

The plots in Figure A.8 through Figure A.13 show some of the data from these mixing tests. Position 3 again represents centerline while positions 0 and 6 represent opposite walls of the combustor. Each data point represents an average over approximately 140 seconds; the error bars represent three standard deviations. Multiple data taken at the same radial position are staggered so that each data point can be seen clearly. Radial O₂ and NO profiles obtained from port 1-1 using the water-cooled probe are plotted in Figure A.8 and Figure A.9 respectively. Data are both spatially and time resolved. O₂ concentrations vary from 10% to 11.5% across the diameter of the furnace with a slight downward shift in concentration between 1:30 and 2:30 p.m. There is no distinct spatial or temporal trend in the scatter of the data. The NO profiles show that time-resolved differences are much more important than any radial variation in NO concentration. One reason for this dramatic shift in NO concentration between 1:30 p.m. and 2:30 p.m. could be an increase in thermal NO production as the continuous firing of coal gradually increases flame temperatures in the combustor. A critical conclusion from both O₂ and NO profiles is that 30 cm below the quarl (the location of port 1-1), the radial gradients in gas phase species' concentrations are small, indicating that the burner does produce a well-mixed coal flame.

Figure A.8 . Port 1-1 radial O₂ profiles taken with water-cooled probe. Fuel is Utah bituminous coal.

Figure A.9 . Port 1-1 radial NO profiles taken with water-cooled probe. Fuel is Utah bituminous coal.

Figure A.10 and Figure A.11 compare radial O₂ profiles in port 3-1 using the quartz and water-cooled probes respectively. In both figures, spatial variations in O₂ concentration are small. In Figure A.11, the spatially resolved data indicate that O₂ concentration is highest near the centerline (4.5%), then drops off to 4% toward the walls. NO profiles for both probes are similar in shape to the O₂ profiles. The conclusion drawn from these two figures is that radial gradients are again small at this furnace location.

The NO concentration profile taken in port 4-4 with the water-cooled probe is plotted in Figure A.12. The standard deviation error bars are very small and the radial profile is basically flat. The O₂ radial profile is also flat. These results indicate that by this location in the furnace, the combustion gases are extremely well-mixed.

Finally, radial temperature profiles were measured in three ports (1-1, 3-1, 4-4) using a 127 μm type R bare wire thermocouple probe while burning a Utah bituminous coal. The bead was coated with slag before the test began, so in reality the diameter of the bead was much larger than 127 μm . The measured temperature profiles are plotted in Figure A.13. Each data point represents a 30 second average. On an absolute scale, all these reported temperatures are too low due to radiation exchange between the bead, the particles, and the combustor walls; for further discussion on this topic and a description of the Type R bare wire thermocouple probe, see "Temperature Measurement" on page 172. Nevertheless, the important information obtained from this plot is not the magnitude of the numbers but that

Figure A.10 . Port 3-1 radial O₂ profiles taken with quartz probe. Fuel is Utah bituminous coal.

Figure A.11 . Port 3-1 radial O₂ profiles taken with water-cooled probe. Fuel is Utah bituminous coal.

Figure A.12 . Port 4-4 radial NO profiles taken with water-cooled probe. Fuel is Utah bituminous coal.

the radial temperature profiles, like the gas concentration profiles, are relatively flat in all ports where temperature was measured.

Thus, based on all experimental data taken at multiple radial positions for a given axial location, the premixed burner produces a flame which is radially uniform.

A.3 Sampling System

A new sampling system was designed and built for the present work in order to obtain accurate NO_x measurements. This section begins with a review of sample probe design followed by a description of the sample probes that were used in the present work. It continues with a discussion of sampling systems for NO_x analysis, and then concludes with an explanation of the new sampling system.

A.3.1 Sample Probes

The designs of most sampling probes reported in the literature are based on convective cooling, water or gas quenching, or aerodynamic quenching techniques. The ideal probe provides a sample that is representative of the gas species' concentrations at the point in the combustor where the probe tip is located. However, according to Heitor and Moreira (1993), the accuracy of measurements taken with sample probes can be influenced by "(1

Figure A.7 . Radial O₂ and NO profiles at port 1-1N using the premixed burner.

probe-induced fluid dynamic disturbances and composition biasing due to nonisokinetic sampling; (2) the efficiency of quenching; (3) the catalytic effects on the probe surface; and (4) the type of averaging given by the probes.” They include multiple references in their paper to studies relating to each of these sources of error.

First, probe-induced disturbances are particularly important if measurements are being taken in a combustor with high axial or radial concentration gradients. In such a case, Heitor and Moreira (1993) suggest that interference effects can be kept as low as 3% if both the probe tip diameter and the upstream diameter of the stream tube entering the probe are smaller than 10% of the characteristic length scale of the flow.

Next, composition biasing can be eliminated by isokinetic sampling. Many researchers have attempted to sample isokinetically in order to reduce this bias (Burkinshaw et al., 1983; Mitchell et al., 1992; Costa et al., 1991b). Nevertheless, isokinetic sampling is not without its problems. According to Tine (1961), the actual behavior of isokinetic probes has revealed some difficulties which reduce their usefulness. A common method for isokinetic sampling is the null-type method. In this method, a differential manometer is used to compare the static pressure of the fluid stream and the static pressure inside the probe. According to the Bernoulli equation, with the assumption of a nonviscous fluid, the velocities are equal when the pressures match. However, head losses can occur within the probe before the static pressure is measured and it is difficult to

Figure A.13 . Radial temperature profiles in a pulverized coal flame measured with a 127 μ m type R thermocouple.

establish the correct position for the static pressure measurement of the undisturbed stream on the outer wall of the probe (Tine, 1961).

Third, the quenching of gas samples extracted from combustion systems is essential to the prevention of chemical reactions occurring in the probe or transfer lines that may significantly alter species concentrations. All of the probe types mentioned above are designed to quench gas samples. Chiappetta and Colket (1984) suggest that aerodynamic quenching probes are the most desirable due to the exceptionally high quenching rates. Nevertheless, they conclude that “the complexities of probe design and construction are more severe than indicated previously.” Heitor and Moreira (1993) report that quench rates of the order of 2×10^6 K/s are easily obtained in water-cooled probes, while researchers at Sandia achieved quench rates of 10^6 K/s with a water-cooled, helium quench probe (Mitchell et al., 1992). Although high quench rates are desirable, attention must also be paid to the sample temperature as it exits the probe due to the presence of condensable vapors such as water. This issue will be discussed in more detail below as it relates to problems with NO_x sampling. Since water-cooled probes are easier to design and build than aerodynamic probes, they would appear to be the probe of choice for combustion sampling. But first, the issue of catalytic effects on the probe surface must be addressed.

Heitor and Moreira (1993) state that fast quenching of combustion gas results in increased rates of radical recombination and promotes the oxidation of NO. They also note that even though metallic probes are recognized to be particularly prone to catalytic activity, catalytic activity has also been observed with quartz probes. Evans et al. (1993) emphasize the importance of minimizing contact with high temperature stainless steel (>394 K) at all points in the sample line, including the probe, to reduce the possibility of NO₂ to NO conversions. In a typical water-cooled stainless steel probe, the inner surface of the probe is maintained at temperatures of 373 K or lower.

Both water-cooled and quartz probes were used in the present work. Since isokinetic sampling is so difficult to achieve, no attempt was made to sample isokinetically. This decision is supported by two conditions specific to the present experiments. First, the use of a premixed burner eliminates large concentration and density gradients that might lead to composition biasing from nonisokinetic sampling. Second, the probes are only being used for gas sampling, not solid sampling. Isokinetic sampling is more critical when sampling solids because the particle size distribution of the collected solid is easily skewed by sampling velocities that are either too high or too low.

The issue of quenching was considered for both water-cooled and quartz probes. Two types of water-cooled probes were designed and built. The first was the water-cooled gas quench probe shown in Figure A.14. The sample is pulled through a 7.7 mm ID stainless steel tube. Helium or nitrogen quench gas is fed into the annular space around the sample tube. This quench gas exits the probe through twelve-0.8 mm diameter holes located near the probe tip. A water jacket comprises the outer two layers of the probe. The 90° bend at the probe tip allows the tip to be aligned such that it faces directly into the furnace flow for accurate sampling at any radial location, although the probe itself will produce some flow

Figure A.14 . Water-cooled gas quench probe. Width scale is double that of length scale to show detail.

field disturbance. Preliminary studies using both helium and nitrogen as the quench gas showed that probe tip temperatures were successfully reduced by the quench gas to temperatures below the 900 K recommendation of Sandia (Mitchell et al., 1992). However, the unfortunate side effect of this quenching was that probe exit temperatures dropped below 373 K. Since NO₂ is fairly soluble in water, sample temperatures should be maintained above 373 K to avoid removal of NO₂ due to water condensation.

The water-cooled gas quench probe was subsequently modified by cutting off the cone (piece F in Figure A.14), removing the inner sample tube with the 12 drilled holes, and replacing it with a piece of undrilled tubing that only extended as far as the end of the water jacket. These modifications left an annular space between the sample tube and the water jacket (formerly the annular space for the quench gas) that is open to the furnace.

This modified water-cooled probe was used for all samples taken in port 1-1. The probe was long enough to extend across the entire radius of the U furnace if desired. Unless otherwise indicated, sampling was done on the furnace centerline. A thermocouple placed at the 90° bend in the probe was used to monitor sample temperature, and thus quench rate, at the probe tip. The highest temperature ever measured was 1220 K, but most temperatures fell in the range from 880-1080 K. This range is slightly higher than the 900 K recommendation, but it represents a trade-off between quenching at the tip and maintaining probe exit temperatures above 373 K. A thermocouple located at the probe exit indicated that sample temperatures ranged from 398-527 K.

The use of quench gas was discontinued for an additional reason. It introduces another source of error- the calculation of the dilution ratio. The quench gas flow can be metered in, but one other measurement, either the total sample flow rate or the concentration of a trace gas, is needed to calculate the dilution ratio. Errors in any of these measurements will result in errors in the dilution-corrected concentrations of gas species. For these experiments, the error introduced by using a quench gas was believed to be greater than any error caused by incomplete quenching at the probe tip.

The second type of stainless steel water-cooled probe consisted of a sample tube surrounded by a water jacket as seen in Figure A.15 (A) and Figure A.15 (B). Both of these probes were used to pull samples from port 6-4W near the U furnace exit. The probe in Figure A.15 (A) was used to take some early coal data. The 90° angle at the tip allowed the probe inlet to face directly into the furnace flow. The sample inlet was located 3.2 cm off of centerline when the probe was pushed in as far as it could go. This probe had to be replaced when the water jacket cracked and began to leak. The probe in Figure A.15 (B) was used next to take a limited amount of both coal and char data before it too had to be replaced due to a leaking water jacket. Because the sample inlet had no bend, it was located perpendicular to the furnace flow. Also, the probe was so short that it only extended in to the edge of the flow area.

There are several causes for concern with these probes. First, neither probe was long enough to sample right on the centerline of the furnace, which is where samples from port

Figure A.15 . Water-cooled gas probes used (A) until 21 Feb 1996 and (B) from 21 Feb 1996 to 26 Apr 1996. Width scale is double that of length scale to show detail.

1-1 were drawn. Also, the probe in Figure A.15 (B) was sampling perpendicular to the flow at the edge of the flow area. These concerns can be allayed by considering the location in the furnace where these probes were used. Combustion is essentially complete by port 4-4, and the radial profiles of gas phase species concentrations are relatively flat at that point (see Figure A.12). Combustion products are extremely well mixed by port 6-4, so radial sampling location and probe tip orientation (parallel or perpendicular to the flow) are unimportant. Figure A.16 is a plot of data taken with the quartz probe described below. The probe tip was situated perpendicular to the flow. The probe was used to sample the furnace flow at several radial locations between centerline and the furnace wall. Radial profiles of CO₂, O₂, and NO_x concentrations are shown in Figure A.16. The NO_x data were taken with the chemiluminescent NO_x analyzer, also known by its brand name TECO. Clearly, sampling location and probe tip orientation are unimportant at this location near the furnace exit.

A second cause for concern with these water-cooled probes is that sample temperatures at the probe exit were typically in the range of 313-328 K, which is lower than the 373 K required to avoid water condensation and NO₂ loss. Although potential NO₂ losses from water condensation in the probe are estimated to be small (<5%), this problem was eliminated by replacing the second water-cooled probe with a quartz probe. Typical probe exit temperatures with the quartz probe are in the range of 475-505 K.

The quartz probe consists of a single piece of quartz tubing that is 50.8 cm long with an OD of 18 mm and an ID of 15.7 mm. It is long enough to extend to the furnace centerline,

Figure A.16 . Effect of sample probe tip location on measured gas phase species concentrations.

and unless otherwise noted, that is where all quartz probe measurements were taken. However, as noted above, location of the probe tip in the flow is not critical. This probe was used for the majority of the coal and char samples pulled from port 6-4. It is connected to the rest of the sample line via a Swagelock fitting that is fitted with a Teflon ferrule.

Since there is no quenching in the quartz probe, an immediate concern is that chemical reactions will continue to occur in the probe. This concern is unnecessary for two reasons. One, centerline furnace temperatures measured with a thermocouple in port 6-4 are in the range of 900-1000 K, which is close to the 900 K post-quenching temperature achieved by the Sandia researchers. Two, as stated previously, combustion is complete by this point, so not many chemical reactions are occurring anyway.

A.4 Sampling System

Getting a sample containing NO_x species from the combustor to the measuring instrument without affecting both total and relative NO_x species concentrations is difficult. Evans et al. (1993) point out that conversion back and forth between NO and NO₂ is well-documented for a variety of sampling conditions, including the catalytic properties of stainless steel to reduce NO₂ to NO. They also note that NO₂ can be lost by absorption into condensed water. One group of researchers has even determined that at elevated temperatures, NO_x in the sample gas can be destroyed (Grove and Samuelsen, 1985). Evans et al. (1993) make the following recommendations to minimize NO/NO₂ conversions and overall NO_x losses: (1) maintain the sample line and any filters at approximately 383 K to avoid condensation and to minimize NO/NO₂ conversions, (2) do not remove water by condensation, (3) use Teflon line and Teflon-coated fittings wherever possible to reduce the catalytic effects of hot stainless steel.

Following these recommendations, the sampling system diagrammed in Figure A.17 was designed and assembled. Each component of this sampling system will be described in the following paragraphs. To begin, the sample exits the probe into a series of stainless steel fittings that include a three-way valve. The purpose of the valve is to allow the sample pump to pull sample either from the furnace or from the room air. This feature is necessary when either heating up or cooling down the sampling system because pulling wet furnace gas through the system at such a time would result in condensation throughout the system. Using stainless steel at this point was unavoidable, but care was taken to minimize the number of fittings. Overall, the sample passes through a 10 cm segment of stainless steel fittings.

The next two components, the glass condenser and the glass flask, were only used with the quartz probe. The heated Teflon line was hooked directly to the three-way valve when the water-cooled probes were used. The purpose of the condenser is to reduce the temperature of the sample exiting the quartz probe sufficiently that the Teflon line does not melt (Teflon begins to soften above 530 K). The glass flask is present to collect any water that might condense from the sample. There is rarely any water in the flask as temperatures generally remain above 373 K. The condenser is wrapped with insulation to prevent excessive heat loss. In the last week of experiments, the condenser and flask were removed from the sampling system and the heated line was hooked directly to the three-way valve at the exit of the quartz probe. This change was

Figure A.17 . Simplified diagram of sample collection system.

made after it was observed that the temperature exiting the quartz probe was rarely hot enough to start softening the Teflon line.

The heated Teflon line between the glass condenser and the quartz glass cyclone was made by running Teflon line through a piece of copper tubing, wrapping heating tape around the copper tubing, and then wrapping the whole ensemble with braided insulation. A thermocouple located in the sample flow at the exit of this heated line is connected to a temperature controller which adjusts power to the heating tape to maintain the setpoint temperature.

The sample exits the heated Teflon line into a heated quartz glass cyclone. The purpose of the cyclone is to remove the larger particulate matter. According to cyclone design calculations, this cyclone is 100% efficient in removing particles 50 μm in diameter and larger. The amount of particulate matter collected in the cyclone depends on the furnace sampling location; significant quantities were collected from port 1-1 samples while very little was collected from port 6-4 samples. The cyclone is wrapped with heating tape and, due to its fragility, placed in an insulated metal box. The temperature measured by a thermocouple placed on the surface of the cyclone is controlled to a setpoint by a second temperature controller.

Upon leaving the cyclone, the sample enters a short segment of Teflon line wrapped with heating tape that serves as a transition between the cyclone and the next component of the sampling system, the heated Teflon filter. The Teflon filter is lined with a 47 mm glass fiber filter which removes any particles 1.0 μm or larger. The glass fiber filter has to be changed several times a day to avoid excessive pressure drop through the filter. The Teflon filter is heated by placing it in a heated, insulated metal box. A third temperature controller controls the temperature measured at the filter surface to a setpoint. The sample is now free of particulate matter.

The sample exits the Teflon filter into a commercially-obtained heated Teflon line. A fourth temperature controller uses a thermocouple located in the sample flow at the exit of the heated line to control to the setpoint temperature. At the exit of this Teflon line, the sample enters a double-headed diaphragm Thomas pump (Model No. 2107CB18TFEL-A). The sample is then pushed out of the pump at a flow rate of 4.75 slpm into two Perma Pure dryers plumbed in series. Heating tape is wrapped around the lines into and out of the pump as well as around the first few centimeters of the first Perma Pure dryer. This final heating tape is controlled by a fifth temperature controller which monitors the surface temperature at the inlet of the Perma Pure dryer. The lines into and out of the pump are plumbed in Teflon while the fittings are stainless steel.

The Perma Pure dryers “utilize a hygroscopic, ion exchange membrane in a continuous drying process to selectively remove water vapor from mixed gas streams. The membrane is a proprietary extrudible dessicant in tubular form” (Perma Pure product literature). A bundle of tubes with a common header is fabricated in a shell and tube configuration. The shell has openings adjacent to the sample inlet and product outlet. If a wet gas stream flows through the tubes and a countercurrent dry gas stream purges the shell, water molecules are transferred through the walls of the tubing from the wet sample gas to the dry purge gas. The dry purge gas gradually becomes wet and exits the shell side at the purge outlet. According to product

literature, “The key to continuous separation of the water vapor from its gas stream is the countercurrent flow.” The membrane in these dryers is also permeable to other compounds with -OH groups (alcohols, etc.), so Perma Pure dryers are not recommended for use with samples containing NH₃, which many times is actually present as NH₄OH. Since NH₃ is not a compound of concern in the char-N experiments, Perma Pure dryers can be used.

Originally, only one Perma Pure dryer was used, but due to significant amounts of water showing up in the FT-IR spectra, the second Perma Pure dryer was added. The two Perma Pure dryers in series are extremely effective at removing water vapor from the sample. Since the water is removed without condensation, there is no loss of NO₂. The dry purge air for the Perma Pure dryers is obtained by pulling room air through a dessicant before the air enters the shell. The wet purge air is then exhausted into the room. The purge air is pulled through the system by an eductor located at the shell exit.

Once the sample has passed through the Perma Pure dryers, it is no longer necessary to heat the sample to avoid condensation. Hence, downstream of the dryers, an unheated piece of Teflon line connects the dryers to a four-way stainless steel valve. This valve is used to send the sample to one of three places: the control room analyzers, the FT-IR, or the room. Both the control room analyzers and the FT-IR will be discussed in subsequent sections. All require that the sample being measured be clean and dry.

NO, NO₂, and N₂O calibration gases were used to test the sampling system for NO_x species loss from the inlet of the first heated Teflon line all the way to the FT-IR. Since the calibration gases are in an inert atmosphere, this test did not detect any NO_x sinks in the sampling system that occur only in oxidizing atmospheres. Results from this test are, however, useful for checking the integrity of the sampling system under inert conditions. The calibration gas concentrations measured by the FT-IR after passing through the sampling system are tabulated in Table A.2.

The relative errors for the various concentrations of N₂O and NO₂ calibration gases are all less than 6%. Only the NO relative error is high at almost 20%, but in absolute terms the difference is only 5.5 ppm. Since the correction curve used by the FT-IR software to quantify NO concentration is more accurate at higher NO concentrations, it is not surprising that this 5.5 ppm difference exists. Clearly, under inert conditions there are no NO_x species sinks from the first heated Teflon line all the way to the FT-IR.

Table A.2 . Check of sampling system with NO, NO₂, and N₂O calibration gases.

Type of Gas	Actual Conc., ppm	Meas. Conc., ppm	Relative Error
N ₂ O	309	298	-3.6%
N ₂ O	20.4	21.3	+4.4%

Table A.2 . Check of sampling system with NO, NO₂, and N₂O calibration gases.

Type of Gas	Actual Conc., ppm	Meas. Conc., ppm	Relative Error
NO ₂	184	191	-3.7%
NO ₂	29.4	27.8	-5.4%
NO ₂	5.6	5.6	0%
NO	28.7	34.3	+19.5%

A.5 Instrumentation/Data Collection

Data from the U furnace were collected at two different locations, the control room and the FT-IR (Fourier Transform Infrared Spectrometer).

A.5.1 Control Room Instrumentation

Three instruments are located in the control room: the O₂ analyzer, the NO_x analyzer, and the CO/CO₂ analyzer. Output signals from these instruments are interfaced to the control room computer. In addition, four type B thermocouple lines from the U furnace were brought into the control room and interfaced to the computer. The type B thermocouples were located in ports 1-1N, 2-1W, 3-1W and 4-2W. Workbench, a data acquisition software sold by Omega Engineering, was used to collect and record both analyzer signals and thermocouple readings.

A Workbench configuration file was specially developed for these experiments. To begin, each instrument signal had to be calibrated within the software so that Workbench recorded the correct gas concentrations in the correct units. This calibration was similar for all three instruments. A zero gas and then a calibration gas were supplied to the instrument. The voltage (or milliamperes) signal read by the Workbench software was recorded for each gas, and then a linear fit to the two data points was input into the configuration file. The end result is that a voltage (or milliamperes) signal from the instrument is converted to the equivalent gas concentration by the software. Next, the software has a built in calibration for thermocouples. It is only necessary to specify the type of thermocouple in the configuration file because the software automatically converts the incoming millivolt signal to a temperature.

Finally, the user must select the sampling rate. Unless otherwise indicated, the sampling rate for all experiments was 1 Hz, which means data were recorded to a log file every one second. Data that were recorded to the log file include: (1) the time; (2) NO, NO_x, CO, CO₂, and O₂ concentrations; (3) port 1-1N, 2-1W, 3-1W, and 4-2W temperatures. In general, the following data logging protocol was used: (1) adjust furnace operating parameters to the desired settings and allow the furnace to come to steady state

(usually 3-5 min), (2) start data logging, (3) log for 3 min, (4) stop data logging. Data in this thesis are reported as an average and a standard deviation for the 3-min logging period unless otherwise indicated.

A.5.2 O₂ and CO/CO₂ Analyzers

The O₂ analyzer used in these experiments was a Yokogawa Zirconia Oxygen Analyzer with an averaging converter system. This instrument was calibrated with a 2.5% O₂ calibration gas as the zero (low concentration) gas and room air as the span gas. It holds its zero (low concentration) gas calibration for at least a week, but if high O₂ concentrations are being measured (>15%), span gas calibration is necessary on a daily basis.

CO and CO₂ gas concentrations were measured by a Nova Model 4280RM Dual Range CO and CO₂ Analyzer. This instrument uses NDIR (nondispersive infrared spectroscopy) technology. The two ranges for CO are 0-1% and 0-10%; the two ranges for CO₂ are 0-3% and 0-30%. The instrument was run with CO set on the 0-10% range and CO₂ set on the 0-30% range. It would have been preferable to run with CO set on the 0-1% range, but no calibration gas was available for that range. The instrument was calibrated with nitrogen as the zero gas and with a 5% CO/12% CO₂ calibration gas as the span gas. The calibration had to be checked on a daily basis (sometimes several times a day) because this analyzer did not hold its calibration very well.

A.5.3 Chemiluminescent NO_x Analyzer

Control room NO_x measurements were made with the Thermo Environmental Model 10A Chemiluminescent NO-NO_x Gas Analyzer, also known as the TECO. When NO reacts with O₃, light emission occurs at a specific wavelength. This chemiluminescence is monitored through an optical filter by a high-sensitivity photomultiplier located inside the instrument. The output from the photomultiplier is linearly proportional to the NO concentration. To measure NO_x concentrations (NO + NO₂), the sample gas is first diverted through an NO₂-to-NO converter before it is reacted with O₃ (Model 10AR Instruction Manual). This NO_x analyzer has multiple linear, full-scale ranges. Depending on the NO concentration in the sample being measured, either the 0-1000 ppm or the 0-2500 ppm scale was used. The instrument was calibrated with nitrogen as the zero gas and three different calibration gases as span gases. If the instrument was set on the 0-2500 ppm scale, the span gas used was a 1320 ppm NO calibration gas. For the 0-1000 ppm scale, a 597 ppm NO calibration gas was used; when it ran out, it was replaced with a 611 ppm NO calibration gas.

The manufacturer claims that the chemiluminescent NO_x analyzer's calibration should vary only 1% of full scale from day to day. In preliminary testing, the calibration was found to vary at least 2% over the course of a day. Also, instrument noise was excessive. For example, with the 597 ppm NO calibration gas flowing through the instrument, the NO output to the computer varied between 575 and 620 ppm. Many efforts were made to

correct these and other problems with the NO₂ analyzer. Only the highlights are reported here.

First, the instrument was shipped back to Thermo Environmental and completely refurbished. Second, the operation of the instrument was modified. Instead of feeding pressurized O₂ to the ozonator by means of a compressed air tank, a tube of dessicant was attached to the ozonator's inlet air line, allowing the ozonator to suck in dried room air as needed. Also, instead of allowing the sample pump to push sample through the instrument, a bypass valve with a rotameter attached was installed in the sample inlet line. Instead of forcing the sample through the instrument, this configuration allowed any sample flow not needed by the instrument to flow through the rotameter bypass to an exhaust line. Third, all three capillary tubes in the instrument were checked and cleaned periodically. Fourth, the five-way valve that is used to select whether zero gas, calibration gas, or sample gas is sent to the instrument was replaced because of leaking seals. Finally, the cause of the instrument noise was traced to degraded oil in the NO_x analyzer vacuum pump. Consequently, the oil was drained and replaced approximately every three weeks when running experiments.

After these changes, the calibration of the analyzer was checked at least twice a day and found to vary less than 1% of full scale. The calibration of the NO_x (NO + NO₂) setting on the analyzer was also checked periodically. The instrument was set on NO mode, and a 191 ppm NO₂ calibration gas was fed through the sample line; the instrument read 1.8 ppm NO. The instrument was then set on NO_x mode with the same calibration gas; the instrument read 184 ppm NO_x. This test was repeated at several different NO₂ concentrations with similar results. The results of this test are plotted in Figure A.18 and indicate that the NO_x setting on the analyzer was functioning properly.

A.5.4 FT-IR

In addition to the data collected in the control room, gas phase NO_x data (NO, NO₂, N₂O) were collected using the FT-IR located adjacent to the U furnace. The FT-IR is a Nicolet Model 550 Magna-IR Spectrometer. It is equipped with an Infrared Analysis M-Series Long Path Cell. The cell has a permanently aligned pathlength of 10 m and a volume of 2.3 liters. The cell body is made of nickel-coated aluminum, the optical coatings are gold, and the windows are silver bromide. The cell is also equipped with a heating jacket, which is used to maintain the cell surface temperature between 375-384 K to prevent water condensation in the cell.

Space limitations preclude a discussion of FT-IR theory in this thesis. Several excellent books exist on the subject, including "Chemical Infrared Fourier Transform Spectroscopy" by Peter R. Griffiths and "Practical Fourier Transform Infrared Spectroscopy" edited by J. R. Ferraro and K. Krishnan. Additional information about trace gas analysis (i.e., pollutants like NO_x species) can be found in "Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems" edited by Ferraro and Basile.

Figure A.18 . TECO NO₂ calibration check.

Discussion in this thesis will focus on the FT-IR operating parameters and calibration methods used in the char-N experiments.

FT-IR operating protocol was as follows. First, the MCT detector was cooled with liquid nitrogen. Next, the bench was aligned and cell optical throughput was checked. If optical throughput was low, the instrument aperture was adjusted. The upper limit of the aperture is determined by the desired resolution. Third, a background spectrum was taken with dry purge air in the cell. Fourth, the settings for the data collection parameters were checked. These parameters were: number of scans = 150, mirror velocity = 3.1647 m/s, resolution = 0.5 cm⁻¹, apodization = Happ-Genzel, zero filling = none, gain = 4.0. Fifth, sample gas was fed into the cell and allowed to purge through the cell for a given amount of time. Once purging was complete, the sample was captured by closing the inlet and outlet valves to the cell. The sample was then allowed to thermally equilibrate. Pressure that built up in the cell as the temperature of the sample increased to that of the cell surface temperature was bled off. Consequently, all samples were taken at local atmospheric pressure. At this point, the sample spectrum was obtained.

Several criteria were used in selecting the data collection parameters. The number of scans represents a compromise between scan time and noise reduction. Approximate scan

time for 150 scans with a mirror velocity of 3.1647 m/s is 190 seconds. The resolution of 0.5 cm^{-1} is the finest resolution achievable with the current FT-IR setup. Resolution of 0.25 cm^{-1} is necessary to obtain a linear response from the FT-IR for some compounds. However, correction curves can be used with compounds that exhibit a nonlinear response at 0.5 cm^{-1} resolution, so 0.5 cm^{-1} resolution is sufficient for most compounds. The mirror velocity is set at the maximum possible because the MCT detector has a very fast response time and thus can handle the high mirror velocities.

Sample purge time and thermal equilibration time are both tricky issues. The sample pump produces a sample flow of approximately 4.7 slpm. Based on a cell volume of 2.3 liters, the entire cell volume should be replaced twice per minute by the incoming sample gas. Throughout most of the char-N experiments, the sample gas was allowed to purge the FT-IR cell for 3 min to insure that the previous sample was completely purged from the cell. This purge time was reduced to 2 min for the final 3 weeks of experiments.

In early experiments, the captured sample was allowed to thermally equilibrate for 5 min or longer. This long equilibration time produced an unfortunate side effect- some of the NO in the sample was converted to NO₂. This effect was noted by comparing NO₂ data from the FT-IR to that from the chemiluminescent NO_x analyzer. Although total NO_x levels measured by the two instruments were almost identical, FT-IR NO₂ concentrations were much higher and NO concentrations were lower than the respective measurements from the chemiluminescent NO_x analyzer. Since no cell pressure buildup was observed after the first 2 min of thermal equilibration, the equilibration time was reduced first to 3 min and later to 2 min. However, even with this reduced equilibration time, some NO₂-to-NO conversion is possible. Hence, although total NO_x levels (NO + NO₂ + N₂O) measured by the FT-IR provide experimental insight, drawing conclusions based on the relative amounts of NO and NO₂ is a futile exercise.

A.5.4.1 FT-IR Calibration

The FT-IR was calibrated using Quant Setup, a quantitative analysis software obtained from Nicolet Analytical Incorporated. Quant Setup uses Classical Least-Squares (CLS) quantitative analysis algorithms, which are ideal for quantifying sample mixtures in which there is little or no interaction between molecules in the sample. Two groups of gases must be included in the Quant Setup method: one, gases to be quantified and two, any other gases in the sample matrix with a high enough concentration to absorb infrared energy. In a fuel-lean combustion mixture, gases with a high enough concentration to absorb infrared energy include CO, CO₂, and H₂O. Consequently, in the method developed for the char-N experiments, six gases were included: NO, NO₂, N₂O, CO, CO₂, and H₂O.

The Quant Setup method requires one spectrum of known concentration (the primary standard) for each gas in the method. Since extrapolation with an FT-IR can introduce errors, the concentration of the calibration standard should be greater than the highest concentration expected in the sample gas. For NO, NO₂, N₂O, CO, and

CO₂, these spectra were obtained using undiluted calibration gases. The FT-IR sampling protocol outlined above was followed for each gas. The H₂O spectrum was obtained by pulling a vacuum on the cell and then injecting 10 μ l of water from a syringe through a septum into the cell. Once the water had vaporized in the hot cell, dry air was allowed to enter the cell until the pressure in the cell rose to local atmospheric pressure. The sample spectrum was then taken.

The next step in method development is to define the analysis regions, i. e. those regions of the spectrum that Quant Setup will use to quantify all the gases (components) in the method. At least one frequency range in which the component peaks are clearly identifiable must be chosen. Several criteria are important in choosing frequency ranges. First, the user must avoid choosing a frequency range in which another component absorbs strongly. If this is impossible, the user can select several small windows within the frequency range in which the component peaks are strong but the interfering peaks are weak. For example, both CO₂ and H₂O interfere in the frequency range of NO absorbance, so several small windows had to be selected in this frequency range. Second, a frequency range in which the component is effectively opaque (absorbance units > 1) is useless (OMNIC QuantPad User's Guide, 1995). This means that for strongly absorbing species such as CO and CO₂ whose concentrations may vary over a wide range, two different analysis regions should be chosen, one for high concentration and the other for low concentration.

Using these criteria, eight analysis regions (frequency ranges) were chosen (COHI, COLO, CO2HI, CO2LO, H2O, NO, NO₂, N₂O). These regions are listed in Table A.3 in the first two columns. A detailed list of the small windows selected within each frequency range is found in Appendix B. Across the top of the table are the names of the eight "components"; COHI and COLO are considered to be separate components, as are CO2HI and CO2LO. The following codes are used in Table A.3:

- Component does not absorb significantly in this region
 - I Component absorbs significantly in this region (i. e. it "interferes")
 - S Use this region to calculate the concentration of this component
- (OMNIC QuantPad User's Guide, 1995).

It is evident from Table A.3 that water interferes in almost every region of the infrared spectrum. The interference is so strong in the analysis region for NO that if most of the water is not removed from the sample prior to FT-IR analysis, the error in the computed NO concentration is unacceptably high. Water interference can also produce large errors in the N₂O concentration. Hence, only dried samples were analyzed by FT-IR.

Figure A.19 is a plot of the NO infrared spectrum in the frequency range that is used by the Quant Setup method to calculate NO concentration. The concentration of

Table A.3 . FT-IR analysis regions for eight components.

Region (cm ⁻¹)		Components in Regions							
Start	End	COLO	COHI	CO ₂ LO	CO ₂ HI	NO	NO ₂	N ₂ O	H ₂ O
732.80	766.57	-	-	S	-	-	-	-	I
907.00	955.00	-	-	-	S	-	-	-	I
1581.0	1632.5	-	-	-	-	-	I	-	S
1849.8	1953.8	-	-	-	I	S	-	-	I
2001.9	2056.7	-	S	I	-	-	-	-	I
2067.8	2133.9	S	-	I	-	-	-	-	I
2180.7	2208.6	I	I	-	-	-	-	S	-
2860.0	2926.3	-	I	-	-	-	S	-	-

the NO calibration gas used to generate this spectrum was 597 ppm. Similar plots of the other components can be found in Appendix B.

Once the analysis regions have been chosen, the final step in the Quant Setup method development is to generate correction curves for species that exhibit a nonlinear absorbance response to concentration. This nonlinearity is evidenced by a calculated concentration based on the calibration gas which differs from the actual concentration by more than a few percent. Since all three NO_x species (NO, NO₂, and N₂O) display nonlinear behavior at a resolution of 0.5 cm⁻¹, correction curves were needed for all three. In order to generate a correction curve, a set of spectra of the component at different known concentrations is needed.

To obtain these spectra, each calibration gas was diluted with varying amounts of N₂. The calibration gas and the dilution gas were each metered by a Brooks Model 5850E Mass Flow Controller (MFC). Flow rate ranges for the two MFCs are 0-1 slpm and 0-10 slpm respectively. The actual concentration of the diluted calibration gas was calculated based on the MFC flow rates of the calibration and dilution gases. The calibration of the 0-10 slpm MFC was checked with a bubble flow meter. At a setting of 2.0 slpm, the measured flow rates for repeat tests were 2.00 slpm and 2.01 slpm. At a setting of 0.5 slpm, the measured flow rates for repeat tests were 0.50 slpm and 0.51 slpm.

Once a set of spectra has been collected, it is analyzed using the primary standard defined in the method. A plot is then generated of measured concentration vs. actual

Figure A.19 . NO infrared spectrum in frequency range used for quantification.

concentration and the data are fit to a polynomial curve. An example of such a plot for NO is seen in Figure A.20. Similar plots for NO₂ and N₂O are found in Appendix A. All three gases were fit to second order polynomial curves. These curves are then used by the Quant Setup method to correct all measured concentrations. Based on the curve fit in Figure A.20, the average absolute error between the corrected and actual concentrations in the set of NO calibration spectra is 1.09% with a range from -3.49% to +1.83%. The average absolute error between the corrected and actual concentrations in the NO₂ calibration set is 1.88% with a range from -3.80% to +3.73%, while that for the N₂O calibration set is 1.57% with a range from -1.89% to 2.40%.

Two other corrections are made by the Quant Setup method. These two corrections are for temperature and pressure. If the sample is taken at a different temperature and pressure than the calibration standards, these corrections are applied. In this work, all samples were taken at local atmospheric pressure; no pressure corrections were applied to any analyses. The error resulting from no pressure correction was estimated by considering the lowest and highest local atmospheric pressure readings during a six month period. If the calibration spectra were taken at the lowest pressure and the sample spectra at the highest pressure, the error in

Figure A.20 . FT-IR correction curve for NO.

measured concentration would be 4.5%. Temperature corrections were applied to all analyses, but since the cell was consistently maintained at temperatures between 375-384 K, these corrections were very small.

The calibration of the FT-IR was checked twice during the course of the char-N experiments. The original calibration was done in December 1995 and January 1996. The NO and NO₂ calibrations were checked at the end of March 1996. The results of this calibration check, found in Figure A.21, show that after two months the calibration of the FT-IR was still accurate. The cell mirrors were recoated in August 1996, and the NO, NO₂, and N₂O calibrations were checked with the recoated cell at the end of August 1996. The results of this second calibration check are plotted in Figure A.22. Clearly, the FT-IR calibration was still accurate seven months later.

A.5.4.2 Comparison of FT-IR NO_x Data to Chemiluminescent NO_x Data

Almost every furnace sample analyzed during the char-N experiments was passed through both the chemiluminescent NO_x analyzer and the FT-IR. Thus, there is a unique opportunity with this data to compare results obtained by the two analytical techniques. Figure A.23 compares NO_x data from the chemiluminescent NO_x analyzer (TECO) to that from the FT-IR. These data were collected between 29 May 1996 and 11 September 1996 from nondoped and doped (all points > 140 ppm NO_x) natural gas flames. Doping refers to the addition of NO or NH₃ into the natural gas line to

artificially raise the level of NO_x in the flame. The FT-IR data are consistently higher with the difference becoming more pronounced as the NO_x concentration increases. However, as a percentage of the total NO_x, this difference is fairly constant. The similarity of the measurements from the two instruments adds a degree of confidence to the results of this study.

Figure A.21 . March 1996 check of FT-IR calibration of NO and NO₂.

Table A.4 shows a comparison of NO_x levels from both instruments for a typical series of tests run on an Illinois char. The first column is an abbreviated description of the test; details on what this abbreviation means are found in Appendix F. The percent difference in total NO_x measured between the two instruments ranges from 5-9% with the exception of the last data point in the table where the difference is over 19%. Similar results were obtained with other experiments and other chars (see Appendix F for NO_x comparisons between the two instruments for all data points). The percent difference was typically less than 10% with the exception of a few data points which all had one thing in common: an Ar/CO₂/O₂ mixture was used instead of air as the oxidant.

The manufacturer of the chemiluminescent NO_x analyzer states that for every 1% CO₂ in the sample gas, the chemiluminescent signal is suppressed by 0.1%. Hence, the NO_x signal would be suppressed 2.5% in a gas containing 25% CO₂. This level of suppression does not account for the large discrepancies in NO measurements between the NO_x analyzer and the FT-IR when using Ar/CO₂/O₂ as the oxidant. Thus, Ar must also suppress the chemiluminescent signal. However, the manufacturer was not sure

Figure A.22 . August 1996 check of FT-IR calibration of NO, NO₂, and N₂O.

Table A.4 . Comparison of NO_x data obtained from the TECO and FT-IR analyzers for a series of tests run on an Illinois #6 char.

Char Type: Ill (22 sept); data collected on 7 June 1996			
	TECO Data	FT-IR Data	% Difference
Sample ID	NO _x , ppm	NO _x , ppm	(FT-IR-TECO)/ FT-IR
14:25 Gas	223	243	8.28%
14:35 Gas'	141	153	7.48%
14:44 Gas+char-baseline	319	340	5.16%
15:01 Gas'+NO-500 ppm	377	404	6.27%
15:09 Gas+char+NO-500	504	546	7.29%
15:17 Gas+NO-500 ppm	488	524	6.82%

Figure A.23 . Comparison of NO_x data as measured by the TECO and FT-IR.

Table A.4 . Comparison of NO_x data obtained from the TECO and FT-IR analyzers for a series of tests run on an Illinois #6 char.

Char Type: Ill (22 sept); data collected on 7 June 1996			
	TECO Data	FT-IR Data	% Difference
Sample ID	NO _x , ppm	NO _x , ppm	(FT-IR-TECO)/ FT-IR
15:47 Gas+NO-900 ppm	814	883	6.67%
16:03 Gas+NO-900 ppm	766	953	7.94%
16:14 Gas'+NO-900 ppm	879	836	7.82%
16:23 Gas+char+NO-900	832	901	7.17%
16:39 Gas+char-15%CO ₂	22	275	19.30%

Figure A.24 . Influence of diluent gas on the accuracy of FT-IR NO measurements.

of the quantitative effect of Ar suppression. Consequently, tests were performed on both the FT-IR and the chemiluminescent NO_x analyzer to measure the effect of Ar suppression.

For the tests, the 1320 ppm NO calibration gas was diluted with varying amounts of a diluent gas; both Ar and N₂ were used as diluents. The gases were metered with the MFCs. The actual concentration of NO was computed based on the flow rates of the calibration gas and diluent gas and then compared to the concentration measured by the FT-IR and by the chemiluminescent NO_x analyzer. The data from these tests are plotted in Figure A.24 and Figure A.25. In Figure A.24, the data collected with the FT-IR show that measured NO concentrations are not affected by the choice of diluent gas; both Ar and N₂ data fall on the same line. Such is not the case with the data from the chemiluminescent NO_x analyzer plotted in Figure A.25. When Ar is used as the diluent gas, the measured NO concentration is as much as 17% lower than the actual concentration. This effect is most pronounced when the Ar to calibration gas ratio is high (lower NO concentrations) since more Ar means more signal suppression.

Due to this Ar-induced chemiluminescent NO_x signal suppression, all NO_x analyzer data obtained from Ar/CO₂/O₂ experiments were determined to be in error. Because a consistent data set with minimal errors was desired for plotting the experimental results, the decision was made to use the FT-IR data set for most plotting.

In the few instances where a TECO data point is considered a necessary or useful addition to a particular plot, its use is indicated.

A.6 Artificial Oxidant System

The equipment that was used to feed various mixtures of Ar, CO₂, and O₂ into the U furnace is collectively referred to as the artificial oxidant system. The major components of this system are diagrammed in Figure A.26.

A.6.1 Description of System Components

The Ar feeding system consists of a liquid Ar cylinder, a cryogenic hose connecting the cylinder to the heat exchanger/vaporizer, a high flow pressure regulator, and a Valtek StarPac Control Valve. The liquid Ar cylinder has an internal vaporizer, but the required Ar flows (285-450 slpm) overwhelm the capacity of the cylinder's vaporizer, resulting in liquid Ar coming out of the vapor valve. This liquid is subsequently vaporized in the large heat exchanger/vaporizer located external to the cylinder. The Ar flow is metered by the Valtek StarPac Control Valve, which is sized large enough to easily handle the required Ar flows; with the setpoint at 434 slpm and the regulator at 207 kPa (gauge), the valve is 55% open. This control valve system has the ability to measure and output flow through the valve based on upstream and downstream pressure values and process temperature (StarPac

Figure A.25 . Influence of diluent gas on the accuracy of TECO NO measurements.

Figure A.26 . Major components of the system for feeding artificial oxidant mixtures of Ar, CO₂, and O₂ to the U furnace.

Intelligent Control Valve System Manual). From the control valve, the Ar flow enters the combustion air supply line to the U furnace.

Prior to use, PID tuning was performed on the control valve in order to minimize response time and maximize stability when changes were made to the setpoint. To operate the control valve, the type of gas flowing through the valve is specified, and then a desired setpoint is chosen. The control valve holds the setpoint extremely well. For example, when the setpoint was 401 slpm, the maximum flow rate in a 5-min period was 406 slpm and the minimum flow rate was 398.5 slpm. At a setpoint of 347 slpm, the maximum flow rate was 348.5 slpm and the minimum flow rate was 345.5 slpm.

The CO₂ feeding system consists of a liquid CO₂ cylinder, a heat exchanger/vaporizer external to the cylinder, a pressure regulator, and a Kammer StarPac Control Valve. As with the Ar system, the external vaporizer is needed to insure that any liquid CO₂ is completely vaporized prior to entering the pressure regulator. This Kammer valve is sized smaller than the Valtek valve; with the setpoint at 87 slpm and the regulator at 207 kPa, the valve is 70% open. It is large enough for the CO₂ flows required for these experiments, which range from 71-147 slpm. The Kammer PID controller was tuned like the Valtek controller. The Kammer control valve also holds the setpoint extremely well. At a setpoint of 100.1 slpm, the maximum measured flow rate was 100.3 slpm and the minimum measured flow rate was 99.9 slpm. The CO₂ flow exits the Kammer valve and mixes with the Ar flow as it enters the combustion air line.

All the components of the O₂ system up to the point where the O₂ is injected into the combustion air line were oxygen cleaned. This includes the regulator, the solenoid valve, the metering valve, the rotameter, the pressure gauge, and all the tubing and fittings in between. The O₂ is fed from cylinders of compressed O₂ hooked up to a manifold. The solenoid valve is a safety feature that prevents O₂ from being fed into the combustion air line when there is little or no Ar and/or CO₂ flow. A pressure sensor in the combustion air line closes the O₂ solenoid valve if pressure in the line drops below a certain level. If there is sufficient pressure in the line, the solenoid can only be opened by depressing the push button switch labeled Supplemental O₂ Solenoid on the main furnace panel (see Figure A.4).

A.6.2 Calibration of Control Valves and O₂ Rotameter

The manufacturer of both the Kammer and Valtek StarPac Control Valves states that a secondary flow measurement device is not necessary because the flow is accurately measured in the valve itself. This claim was checked by flowing the appropriate gas (Ar or CO₂) through the control valve (Valtek or Kammer respectively, which maintained the flow at a specified setpoint. The outlet of the control valve was plumbed to the inlet of the large Brooks rotameter used to meter the main combustion air. The flow rate through the Brooks rotameter was estimated based on the float position and the pressure in the rotameter; a density correction was applied (see equation (1)) since the rotameter was calibrated with air, not Ar or CO₂. The results of this control valve flow rate check are found in Figure

Figure A.27 . Check of Valtek control valve calibration using Ar gas.

A.27 and Figure A.28. There is considerably more variation between the Ar flow as measured by the control valve and the rotameter than there is between the two CO₂ flow measurements. The percent difference between the Valtek and rotameter Ar flow measurements ranges from 2.0-8.5%. The percent difference between the Kammer and rotameter CO₂ flow measurements ranges from 0.9-3.9%. These results provide an estimate of the error in the Ar and CO₂ flow rates measured by the control valves.

The O₂ rotameter, a Dwyer Series RMC, was not calibrated with O₂ for obvious reasons. Also, since it had been oxygen cleaned, its calibration could not be checked with air. Hence, flow rates through the rotameter were estimated from the float position and the pressure in the rotameter with a correction made for the density of O₂ (the rotameter was factory calibrated with air) according to equation (1).

A.6.3 Artificial Oxidant System Protocols

The following protocol was established for the use of the artificial oxidant system. First, a U furnace spreadsheet is used to determine the required settings (float position and pressure) for the O₂ rotameter and the required setpoints for the Ar and CO₂ control valves. The spreadsheet computes the required O₂ based on the firing rates of the fuels and the desired stoichiometry. Then the required flow rates of Ar and CO₂ are computed based on the percentages of O₂, Ar, and CO₂ desired in the artificial oxidant mixture. In all

Figure A.28 . Check of Kammer control valve calibration using CO₂ gas.

experiments conducted for this thesis, the O₂ concentration in the artificial oxidant was held constant at approximately 20.9%.

Once the settings are determined, the liquid Ar and liquid CO₂ cylinders are opened and the control valves are set at the setpoints shown in the spreadsheet. With Ar and/or CO₂ are flowing into the combustion air line, the O₂ cylinders are opened, the Supplemental O₂ solenoid is opened, and the metering valve is adjusted until O₂ begins to flow. The float position and pressure in the O₂ rotameter are adjusted using the metering valve until the flow rate matches that given by the spreadsheet. A sample of the mixture is then analyzed using the O₂ and CO₂ analyzers in the control room. If the percentages of O₂ and CO₂ measured by the instruments do not agree with the desired concentrations input in the spreadsheet, the CO₂ and Ar setpoints are adjusted slightly until the measured percentages agree with the spreadsheet percentages. As an example, the desired O₂ concentration is 20.9% and the desired CO₂ concentration is 15%. The measured concentrations are 20.1% and 14.5% respectively. The Ar setpoint is decreased and the CO₂ setpoint is slightly increased until the measured and desired concentrations match. For almost all data points, the actual setpoints never varied more than +/-5% from the spreadsheet setpoints.

Finally, when operating the artificial oxidant system, a stream of Ar (approximately 4.7 slpm) was fed to the top of the hopper of the Ktron coal/char feeder. The purpose of this Ar stream was to fill the gas pocket between the top of the char bed and the lid of the

Figure A.29 . Comparison of theoretical NO_x predictions to measured NO_x predictions in an NO-doped natural gas flame. Oxidant is Ar/CO₂/O₂.

hopper with Ar. Thus, if the suction of the eductor pulled any gas through the bed and into the char feed line, that gas was Ar and not air.

A.7 NH₃ and NO Addition

Some char-N experiments required that a known level of NO_x be present in the flame zone. This NO_x doping was achieved by injecting either NH₃ or NO gas into the natural gas just prior to the gas entering the burner. The NH₃ and NO gases were metered into the natural gas stream with the same MFCs that were used to calibrate the FT-IR.

The MFCs plugged up several times, so they had to be opened up and the orifice inside cleaned out. The cause of the plugging was the formation of ammonium nitrate crystals in the orifice; these crystals formed because one gas was not completely purged from the MFC before the other gas was fed. The calibration of the MFC can be slightly altered anytime the MFC is opened, so the MFCs were not used for FT-IR calibration again until they had been recalibrated at the factory.

If the feed rate of NH₃ or NO gas is computed based on the flow rate of the combustion products and the desired concentration of NO_x in those combustion products (assuming 1 ppm NH₃ or NO fed = 1 ppm measured), the measured NO_x will never equal the theoretical (or computed) NO_x. This fact is illustrated by the FT-IR data plotted in Figure A.29. These data were taken using Ar/CO₂/O₂ as the oxidant with NO as the doping gas. The only source of NO_x in this system is the NO gas. As the feed rate of NO gas increases, the ratio of measured NO_x to theoretical NO_x decreases. This decrease results from reduction of NO to N₂ in the flame zone

due to the presence of hydrocarbon radicals; the reduction rate increases with increasing NO concentration. NH₃ can also undergo oxidation and/or reduction reactions to form NO_x species or N₂ respectively.

Because measured NO_x does not equal theoretical NO_x when injecting either NH₃ or NO, all experiments were based on measured NO_x. As an example, if the experiment called for 900 ppm NO_x in the flame zone, the setpoint of the NO gas MFC was adjusted until the NO_x concentration in the sample being drawn from the furnace (as measured by the chemiluminescent NO_x analyzer) reached approximately 900 ppm.

A.8 Temperature Measurement

Temperature measurement in combustion systems is a very complex issue, especially when particles are present because the gas and the particles are not generally at the same temperature. A brief discussion of common gas and particle temperature measuring techniques along with their advantages and disadvantages is presented here.

A.8.1 Gas Temperatures

Gas temperatures are most commonly measured using thermocouple probes; thermocouple probes include both bare fine wire thermocouples and aspirated thermocouples like the suction pyrometer (Chapter 2 in Smoot, 1993). Thermocouple types made of platinum-rhodium alloys are suitable for flame temperature measurement.

The principle advantages of bare fine wire thermocouples are (1) measurements can be made with the high precision characteristic of electrical measurements, (2) small thermocouples can be constructed so that disturbance to the flame is minimized and high resolution is obtained, and (3) the method is simple, convenient, and relatively inexpensive (Beer and Chigier, 1972). However, several sources of error must be accounted for including radiative heat transfer between the combustor walls and the thermocouple bead, conduction heat transfer along thermocouple leads, and catalytic reactions on the bead (Chapter 2 in Smoot, 1993). If particles are present, radiative heat transfer between the particles and the bead and coating of the bead by the particles are sources of error. Hence, in general, the thermocouple does not obtain the same temperature as the hot gas.

Some of these errors can be minimized. For example, in an excellent review article, Heitor and Moreira (1993) conclude that catalytic heating can be reduced by coating the wires with a suitable noncatalytic material while conduction heat losses are negligible for thermocouple wires whose length-to-diameter ratios are above 200. Also, zones where catalytic heating is most pronounced (regions with large concentrations of unburned fuel) can be avoided.

Other errors such as heat losses from radiation and conduction can be corrected using standard methods proposed by Bradley and Matthews (1968) and Kent and Bilger (1973). Nevertheless, heat loss corrections can be difficult because they require information on the

combustor wall temperatures and on the physical properties of the thermocouple and gas, many of which must be estimated. Consequently, one researcher has suggested a method for measuring gas temperature with thermocouples that requires no corrections (De, 1981). The method requires that the gas temperature be measured in the same location by three thermocouples of different, known diameters. Another approach, as described by Hassan et al. (1983), is to minimize radiative heat losses from the bead by minimizing the size of the bead. When taking measurements in a gas-fired furnace, they estimate that the temperature measurement error due to radiation loss from a 40 μm Pt/Pt-13%Rh thermocouple is no more than $\pm 30^\circ\text{C}$. Using the method of De in a fuel oil-fired furnace, Costa et al. (1991a) estimate that this same 40 μm thermocouple measures a temperature within 10% of the “true” temperature.

In suction pyrometers, the thermocouple is shielded from its surroundings by refractory shields, minimizing the gain or loss of radiant heat. In addition, hot furnace gas is drawn over the sheathed thermocouple at high suction velocity, making convection the dominant form of heat transfer from the gas to the thermocouple (Beer and Chigier, 1972). The magnitude of the suction velocity is the most important parameter to insure that the heat transfer coefficient (and thus convection heat transfer) is maximized. A value of 200 m/s is recommended (Heitor and Moreira, 1993). The suction pyrometer eliminates the need for radiation corrections, but it is not without its drawbacks. The main drawback is its bulky size, which can disturb the flow. Goldman (1987) suggests several designs for minipyrometers to minimize the flow disturbance effect. An excellent discussion of the theory of and sources of error with suction pyrometers is found in Chedaille and Braud (1972).

Gas temperatures can be measured more accurately using nonintrusive optical techniques such as anti-Stokes Raman spectroscopy or Rayleigh and Raman thermometry. However, these methods are generally limited to use in carefully controlled, small scale laboratory environments (Chapter 2 in Smoot, 1993).

A.8.2 Particle Temperatures

Particle temperatures in flames are most commonly determined based on radiative emission measurements with a pyrometer (Chapter 2 in Smoot, 1993). Two-color pyrometry, which measures radiation over two narrow, distinct wavelength bands, has been used quite frequently (Ayling and Smith, 1972; Tichenor et al., 1984; Schroeder et al., 1992), although some work has been done with four-wavelength pyrometers (Altenkirch et al., 1984; Mackowski et al., 1983). Particle temperature measurement has also been combined with particle size and velocity measurements in sophisticated optical systems (Tichenor et al., 1984; Fletcher et al., 1989; Schroeder et al., 1992). With all these pyrometers, wavelengths are chosen to be in transparent regions of the emitting gases.

Several sources of error must be considered when making radiative emission measurements from particles. First, radiant energy can be scattered by the particles (either into or out of the line of sight of the pyrometer) such that the total radiation received by the

pyrometer is the sum of emitted plus scattered or reflected radiation. One group of researchers solved this problem by using a mathematical model coupled with on-line computation to account for the effects of scattering (Marr et al., 1990). Other researchers avoid the problem by taking measurements in dilute particle concentrations such that particle effects on each other are negligible (Tichenor et al., 1984; Fletcher, 1989; Schroeder et al., 1992). Mackowski et al. (1983) state that sophisticated radiation modeling is not needed for optically thin, laboratory scale, pc flames because scattering is unimportant. Butler (1992) concludes that even in measurements taken in dense particle clouds in full scale boilers, errors due to scattering are much smaller than errors caused by soot.

Hence, a second source of error which must be considered is the attenuation of radiant energy intensity due to absorption and emission by soot, whose concentration and optical properties are unknown (Mackowski et al., 1983; Butler, 1992; Altenkirch et al., 1984). Based on a theoretical study by Grosshandler (1984) on the effect of soot on pyrometric measurements at different wavelengths, Fletcher (1989) and Schroeder et al. (1992) chose pyrometer wavelengths which minimized interference by soot and/or tar clouds surrounding the particle. Butler (1992) suggests that in industrial-type pc flames, the uncertainty estimate for temperature measurements made outside the reaction zone is 80 K (the pyrometric measurement is always high) while the error rises to 200 K for measurements made in the near-burner region.

Finally, the meaning of particle temperature when measuring emitted radiation from a particle cloud is unclear because all particles are not at the same temperature. Although researchers have successfully measured particle temperatures in dilute particle concentrations in the laboratory, the application of these techniques to full scale pc flames is difficult for reasons stated above. Because of all the difficulties associated with particle temperature measurement and with the interpretation of what a particle cloud temperature really means, particle temperatures were not measured in the present work.

A.8.3 Temperature Measurement in the U Furnace

Because of the difficulty and expense of obtaining optical temperature measurements, thermocouple probes (fine wire thermometry and suction pyrometers) were used for all temperature measurements in the U furnace. A preliminary fine wire thermocouple study was conducted in the natural gas-fired U furnace with three different diameters of type R (Pt/Pt-13% Rh) wire similar to the work of De (1981). The main difference is that in De's work, the three thermocouples were mounted in the same probe, while in this work each diameter of wire was mounted in a separate thermocouple probe consisting of a 61 cm length of double-bore ceramic tubing with half of that length encased in a piece of 0.64 cm OD stainless steel tubing. The wire was threaded through the double bore tube leaving only the bead extending from the end of the tube; this configuration is referred to as a bare tip. The beads had approximately the same diameter as the corresponding wire. Each bare wire probe was then inserted into the same port in the U furnace and the temperatures at

radial positions 1, 3, 5, 3 (or 4), and 1 were measured (as mentioned previously, radial positions 0 and 6 correspond to the walls while radial position 3 corresponds to centerline).

The results of this study are shown in Figure A.30 for temperatures measured in ports 2-3 and 4-4. Each point represents a 3-min average. When the three bead sizes and their corresponding temperature measurements are input into De's formula for the "true" temperature shown below, the results are inconclusive.

$$T_f = \frac{\left(T_1 - \sqrt{\frac{d_1}{d_3}} \times T_3\right) - \left(T_1 - \sqrt{\frac{d_1}{d_2}} \times T_2\right) \times (T_1^4 - T_3^4) / (T_1^4 - T_2^4)}{\left(1 - \sqrt{\frac{d_1}{d_3}}\right) - \left(1 - \sqrt{\frac{d_1}{d_2}}\right) \times (T_1^4 - T_3^4) / (T_1^4 - T_2^4)} \quad (2)$$

For example, using the temperatures of 1372 K, 1363 K, and 1366 K measured at radial position 1 in port 4-4 by the 51 μm , 76 μm , and 127 μm bare wire probes respectively, the calculated "true" temperature is 1367 K. There are two reasons for these inconclusive results. One, the largest bead size (127 μm) does not measure the lowest temperature, which it theoretically should. Two, even though the 127 μm bead is more than double the size of the 51 μm bead, the difference in temperatures measured by the two thermocouples is only 9 K, which is theoretically too small. The results in Figure A.30 do show that measured temperatures in this gas-fired furnace are not a function of the amount of time the thermocouple has been exposed to the furnace flow, i.e., the temperature measured at position 1 at the beginning of the test is the same temperature measured at position 1 at the end of the test.

This fine wire thermocouple test was repeated while firing the U furnace with a Utah bituminous coal. For the coal test, the 51 μm wire type R thermocouple probe was replaced with a 256 μm type B (Pt/Pt-30% Rh) probe. Temperature measurements taken in port 4-3 are plotted in Figure A.31. De's equation could not be applied to these results because the method requires that all three beads be of the same type. However, the method would be difficult to apply anyway because ash buildup on the bead affected the measured temperature. Unlike the results from the natural-gas fired furnace, measured temperatures were a function of the amount of time the thermocouple had been in the furnace. As noted by other researchers who have used bare wire thermometry in coal-fired combustors (Hassan et al., 1985), the wires quickly become coated with ash deposits, which affects the radiation error. In Figure A.31, as the bare wire probe is moved from radial position 3 to 5 and then back to 3, the measured temperature drops by approximately 20 K between the first and second measurements at position 3 for all thermocouple bead sizes. The same is true at position 1. The change in bead size resulting from ash deposits on the bead make radiation corrections difficult to compute.

Figure A.30 . Radial temperature profiles measured in the natural gas-fired U furnace with three diameters of thermocouple wire.

The effect of ash deposition on the bead is seen again in Figure A.32. In this experiment, the U furnace was fired with a Utah bituminous coal and radial temperatures were measured in port 2-3. Three different thermocouple probes were used: a 127 μm type R bare wire probe, a 256 μm type B bare wire probe, and a 127 μm type R probe with a covered tip. The covered tip probe was made the same way as the bare wire probes except that high temperature refractory cement was molded around the exposed bead to completely cover it up. Temperatures at radial positions 1, 3, 5, 3, and then 1 were measured and the data plotted in Figure A.32. The covered tip thermocouple temperatures were initially 20 to 50 K lower than those measured by the bare wire thermocouples, but as ash deposited on the bare wire beads, the measured temperatures decreased. The second time the temperatures at radial position 1 were measured (at the end of the test), all three

Figure A.31 . Radial temperature profiles measured in the coal-fired U furnace with three diameters of thermocouple wire.

Figure A.32 . Radial temperature profiles measured in the coal-fired U furnace with three different thermocouple probes.

probes were within 20 K of each other and the type B bare wire probe actually read lower than the type R covered tip probe.

An attempt to quantify the radiation correction for various operating conditions was made by Hirji (1986) in his Ph.D. thesis. He made estimates of the various physical data related to the gas and the bead that are required in the steady state energy equation and then solved the equation for a variety of conditions. The results of these calculations are plotted in Hirji's thesis as the influence of thermocouple diameter on the radiation correction, the influence of velocity on the radiation correction, and the influence of wall temperature on the radiation correction. At a thermocouple temperature of 1500 K and wall temperature of 1200 K, the radiation correction for a bead diameter of 100 μm is estimated to be 70 K while that for a bead diameter of 400 μm is 190 K.

Another potential problem with the use of fine wire thermometry in particle-laden flows is that the wires are very delicate and thus easily broken. In the preliminary testing phase with different diameters of both type R and type B thermocouples, none was robust enough to last very long in the furnace without one of the wires breaking. Since it is both costly and time-consuming to be continually replacing thermocouple beads and wires, an alternate thermocouple probe design was implemented. This design consists of a 61 cm length of double bore ceramic tubing (2.9 mm OD) slipped inside a second piece of ceramic tubing (4.8 mm OD, 61 cm length). Half the length of the outer ceramic tube is encased in a piece of 6.4 mm OD stainless steel tubing. Type B thermocouple wire of diameter 203 μm is then threaded into the double bore tubing until only the bead extends from the end of the double bore tubing. The double bore tube is then recessed slightly in the outer ceramic tube such that the thermocouple bead does not protrude past the end of the outer ceramic tube. Refractory cement is then used to fill in the recessed volume containing the bead. The end result is that the bead is effectively shielded from the flame by a layer of refractory cement.

There are several advantages to this design. First, the double layers of ceramic add robustness while shielding the bead from particle-laden gases. This probe can be left in port 1-1 of the U furnace for several days before repair work is needed. Second, using type B wire insures that temperatures at any furnace location can be measured. Type B wire is recommended for continuous use with temperatures up to 1977 K while type R wire is only recommended for temperatures up to 1671 K. Third, conduction errors are minimized because a single piece of wire extends from the bead back to the lead, a length of approximately 65 cm. The big disadvantage with this design is that radiation errors are greatly increased because of the relatively large diameter (6.4 mm) of the outer ceramic tube which encases the thermocouple bead. Also, ash and/or slag buildup on the ceramic tube increases the tube diameter over time and has an insulative effect on the bead.

In order to overcome some of the disadvantages of this thermocouple probe design, a second method of temperature measurement, the suction pyrometer, was employed. As stated previously, the suction pyrometer eliminates the need for a radiation correction because the bead is shielded from radiant heat loss or gain by ceramic sheaths and because

the primary form of heat transfer to the bead is convection. The suction pyrometer designed and built for use in the U furnace is shown in Figure A.33. The main body of the pyrometer, made of all stainless steel, consists of a water jacket, an annular ring through which the hot gas is pulled, and the innermost tube in which the thermocouple wires are located. The triple-layer ceramic tip assembly, purchased from IFRF, is inserted into the main body until it rests against the stainless steel ring shown in Figure A.33, Detail 1. Type B thermocouple wire (203 μm) is threaded through the double bore ceramic. Refractory cement was originally applied around the base of the outer ceramic tip where it entered the water-cooled main body, but the tip repeatedly broke off at that location. Since the fit between the ceramic tip and the main body was fairly snug, the application of the refractory cement was eliminated and, as a result, tip breakage at that location was reduced.

This suction pyrometer is large enough to cause flow disturbances in the U furnace. However, since the premixed burner produces a relatively flat radial temperature profile (see Figure A.13), flow field disturbances are not a significant source of error. Because convection is the principal form of heat transfer in the suction pyrometer, the critical parameter is suction velocity. The estimated suction velocity in this pyrometer is 180-210 m/s, depending on sampling location, which is near the 200 m/s recommended by Heitor and Moreira (1993). Consequently, temperatures measured by the suction pyrometer are estimated to be within 100 K of the true gas temperatures.

The suction pyrometer was never used to measure temperatures in particle-laden flows because slag quickly clogs the suction channels and the whole ceramic tip has to be replaced. Even in natural gas-fired flames, the suction pyrometer is very fragile and time-consuming to operate. Thus, the following protocol was developed for temperature measurement in the U furnace. On days when experimental data were logged, the suction pyrometer was used to take centerline temperature measurements in three or four ports (1-1N, 2-1W, 3-1W, 4-2W) while firing with natural gas. This was typically done before any other data were taken. Once the suction pyrometer data were logged, thermocouple probes were reinserted into those same ports (1-1N, 2-1W, 3-1W, 4-2W) with their tips at centerline; those probes were then used for temperature logging the remainder of the day. An estimate of the error in the thermocouple probe measurements is made by comparing the suction pyrometer temperature measurement to the probe measurements logged just before and just after the suction pyrometer reading is taken. Embedded in this error estimate are the effects of wall temperature, gas temperature, probe diameter, and other physical properties.

Figure A.34 and Figure A.35 compare suction pyrometer temperatures to thermocouple probe temperatures logged just prior to and just after the suction pyrometer temperatures at four different ports. These plots contain only a sampling of available data. Additional data are found in Appendix F. Each data point represents a 3-min average.

Several observations should be made regarding these plots. First, the temperatures measured by both the suction pyrometer and the thermocouple probes are remarkably consistent. As an example, in port 2-1, suction pyrometer temperatures vary between 1745

- Suction pyrometer
- Thermocouple probe (before s.p.)
- ▲ Thermocouple probe (after s.p.)

Figure A.35 . Comparison of suction pyrometer temperature measurements to thermocouple probe temperature measurements at two furnace locations: (a) Port 3-1, (b) Port 4-2.

Figure A.33 . Suction pyrometer used to measure temperatures in the U furnace.
Detail 1 and Detail 2 are included for completeness.

Figure A.34 . Comparison of suction pyrometer temperature measurements to thermocouple probe temperature measurements at two furnace locations: (a) Port 1-1, (b) Port 2-1.

K and 1795 K while thermocouple probe temperatures vary between 1535 K and 1590 K. Because the data are consistent, the proposed method of error estimation based on the difference between the suction pyrometer and thermocouple probe measurements seems reasonable.

Second, probe temperatures logged just before the suction pyrometer measurement are in general slightly lower than probe temperatures logged just after. The probable reason is that before the probe was reinserted in the furnace, ash and/or slag that had built up on the probe over the course of the previous day's experiments was physically scraped off or it popped off as it cooled. Since ash and slag have an insulative effect on the probe tip, removal causes the measured temperature to rise slightly. The most dramatic example of the effect of ash and slag is seen with the 1 March data in port 1-1. The outer ceramic sheath on the thermocouple was replaced between the two probe measurements with the result that the second probe measurement is 100 K higher than the first. This new sheath was rapidly coated with an ash/slag layer and measured temperature dropped from 1760 K to 1690 K within half an hour.

A final question should be addressed. In particle-laden flames, what temperature is actually being measured by the thermocouple probes? Because of the complexity of such a system, radiative heat transfer between gases, particles, combustor walls, and the thermocouple bead is occurring simultaneously. Hence, the temperatures recorded for particle-laden flows in Appendix F represent some ensemble average of gas and particle temperatures at the location the temperature measurement was made.

B. Appendix B - Collection and Characterization of Coal Chars

B.1 Characterization of Parent Coals

Five coals of various rank were selected for this study. The list of five coals including their respective rank and the supplier is as follows: (1) Illinois #6, a high-volatile C bituminous coal obtained from Consol; (2) Pittsburgh #8, a high-volatile A bituminous coal also obtained from Consol; (3) Utah, a high-volatile bituminous coal obtained from the Huntington Canyon mine in Utah; (4) Knife River, a North Dakota lignite obtained from the University of North Dakota Energy and Environmental Research Center (UND-EERC); (5) Black Thunder, a Powder River Basin Wyoming subbituminous coal also obtained from the UND-EERC. All coals were pulverized to a standard power plant grind of at least 70% through -200 mesh. The coals received from Consol and UND-EERC were pulverized at those respective facilities. The Utah bituminous coal was pulverized by Vortec Products Company, Long Beach, California. Particle size distributions for all the coals except Black Thunder are included in Appendix C along with a description on how the distributions were determined.

Proximate and ultimate analyses were performed on these five coals. The results of these analyses are tabulated in Table B.1 and Table B.2. All coals except Black Thunder were analyzed by Huffman Laboratories, Golden, Colorado. The Black Thunder coal was analyzed by UND-EERC. It should be noted that since the Knife River coal was dried in large trays in a drying oven prior to being burned in the U furnace, the Knife River coal analyses were performed on a sample of this dried coal. In Table B.2, the weight percent oxygen was

Table B.1 . Proximate analyses of parent coals.

	Moisture (%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)	Calorific Value (kJ/kg)
Coal	as rec'd	as rec'd	as rec'd	as rec'd	as rec'd
Utah	2.46	7.89	41.93	47.72	29685
Pittsburgh #8	1.72	8.06	36.65	53.57	30924
Illinois #6	6.91	5.56	46.38	41.15	29343
Knife River	21.9	8.77	58.32	11.01	19509
Black Thunder	20.1	4.95	34.36	40.59	21358

determined by difference. The nitrogen content of the coals (dry basis) ranges from 0.84% for Black Thunder to 1.76% for Illinois #6. The column labeled “%N after vol.” in Table B.2 refers

Table B.2 . Ultimate analyses of parent coals.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	% N after vol.
Coal	dry	dry	dry	dry	dry	
Utah	71.44	5.11	1.39	0.59	13.38	1.37
Pittsburgh #8	75.21	4.91	1.6	0.9	9.18	1.17
Illinois #6	75.85	4.98	1.76	0.92	10.52	1.11
Knife River	62.81	4.24	0.92	1.32	19.48	0.76
Black Thunder	67.32	4.77	0.84	0.50	20.36	n/a

to the nitrogen content of the coal after the volatiles test had been completed, i.e., the nitrogen content in the char. These nitrogen contents can be compared to the nitrogen contents of the coal chars which will be discussed shortly.

B.2 Collection of Coal Chars

One goal of these experiments was to work with chars which were prepared at pc conditions so that any data collected would be most relevant to the pc regime. Hence, the chars were prepared by feeding coal to the U furnace via the premixed burner and then collecting the coal from the furnace after it had partially burned. Details of the char collection process and of furnace operating parameters are included in this section.

B.2.1 Char Collection System Components

Figure B.1 is a schematic diagram of all the components of the char collection system. The collection system was designed to be inserted into any port in Section 1 or 2 but was used almost exclusively in port 1-1 for reasons explained shortly. The collection system had three purposes: (1) to quench gas and particle combustion reactions as the particle-laden combustion gases exited the furnace; (2) to collect partially burned chars as quickly and efficiently as possible; (3) to cool the combustion gases to less than 340 K prior to entering the vacuum pump. Each component of the system served one or more of these purposes.

The first component of the system was a water-cooled plate which was later replaced with a piece of insulation board. This plate (or board) was inserted into port 1-1S until it extended across the diameter of the furnace to the edge of port 1-1N. This plate (or board) effectively covered the entire cross section of the furnace so that particle-laden gases were forced out of port 1-1N. The next component, the stainless steel quench gas injector shown

Figure B.1 . Schematic diagram of the entire char collection system.

Figure B.2 . Quench gas injector inserted into port 1-1S. (Detail A from Figure B.1).

furnace flow as it exited through port 1-1N. The flow rates of both air and N₂ were controlled using the Valtek StarPac Control Valve described in “Artificial Oxidant System” on page 166. Quench air was obtained from a regulated high pressure air line in the laboratory. N₂ gas was obtained from a cylinder of liquid N₂. A vacuum pump located at the end of the char collection system insured that the flows from the burner and from port 1-1S were directed out port 1-1N. Additionally, the damper located in the furnace exhaust line was closed while collecting char, thus minimizing any vacuum in the furnace downstream of port 1-1.

A stainless steel sleeve was inserted into port 1-1N to protect the exposed layers of insulation board in the port and the carbon steel at the port opening from being corroded by the combustion gases as they exited the furnace. This sleeve was part of an assembly that also included three water-cooled sections (labeled “Water-Jacketed Cooling Section” in Figure B.1); the entire assembly was bolted to port 1-1N. The purpose of these three sections was to further cool the particle-laden combustion gases prior to the cyclone. The water jackets of all three water-cooled sections contained baffles which directed the water for maximum circulation. In addition, cooling fins located around the inside circumference of each section extended 1.5 cm into the flow for the length of the section. The first and third water-cooled sections were transition pieces. The first piece made the transition from the 17.8 cm by 7.6 cm furnace port opening to a circular opening of diameter 6.4 cm; its length was 21 cm. The third piece made the transition from the 6.4 cm diameter circular opening to the 7.6 cm by 3.8 cm cyclone opening; its length was also 21 cm. The middle piece had a circular cross section with an ID of 6.4 cm; its length was 51 cm.

An air-atomized water spray nozzle was mounted onto port 1-1N between the furnace wall and the flange. A hole was drilled through both the port wall and the stainless steel

sleeve so that the water spray would reach the hot combustion gases. This nozzle was used as a secondary form of quenching during some of the char collection experiments. It was used infrequently because it caused a rapid buildup of particles in the throat of the port where the spraying occurred.

The next component in the char collection system was the cyclone. The dimensions of the cyclone inlet were 7.6 cm by 3.8 cm. The main body of the cyclone was 61 cm long with that length equally divided between the constant-diameter top half and the tapered bottom half. The diameter of the top half of the cyclone was 15.2 cm while the diameter of the exit was 7.6 cm. The entire cyclone was constructed from carbon steel sheet metal. The cyclone was designed to remove particles of diameter 50 μm and larger with an efficiency of 99.99% and particles of diameter 10 μm with a 96% efficiency. In practice, removal efficiencies were significantly lower. The char particles were collected in a removable steel bucket that was bolted onto the bottom of the cyclone. This bucket was unbolted and emptied several times a day during the char collection experiments.

Immediately downstream of the cyclone was a 1.4 m long section of 7.4 cm OD carbon steel pipe followed by a tee. A air-atomized water spray nozzle was mounted on the top of the tee and a PVC water knockout pot was attached to the bottom of the tee. Thus, any water spray that was not vaporized in cooling the combustion gases was collected in the knockout pot and was continuously removed through the water drain line.

The final two components in the char collection system were the steel-ribbed flexible hose and the Doerr vacuum pump. The flexible hose connected the knockout pot to the pump. The Doerr vacuum pump exhausted to the fiberglass flue duct running through the laboratory. The pump had sufficient capacity for the needs of the char collection system. It consistently pulled an estimated 1250 slpm through the system when char was being collected.

Initially, a refractory choke was inserted into ports 1-1N and 1-1S and the char collection system was set up in port 1-2. However, burnout was nearly complete by port 1-2, in part due to the fact that the refractory choke created a region of intense combustion between the premixed burner and port 1-1. Consequently, the refractory choke was removed and the char collection system was set up in port 1-1.

B.2.2 Furnace Operating Parameters during Char Collection

The principal concerns during char collection were twofold: one, to maintain a well-mixed coal flame burning at pc conditions and two, to safely collect char. In order to maintain a self-sustaining coal flame, the secondary air had to be preheated by the electric heaters. Temperatures measured in the middle of the premixed burner's mixing chamber were in the range 390-450 K for all coals except Black Thunder. Because of difficulties in maintaining a flame with Black Thunder coal, the electric heater setpoints were raised until temperatures in the burner's mixing chamber reached 505 K. Even at these elevated temperatures, sustained ignition of the Black Thunder was difficult. Consequently, it was

cofired with natural gas (10-20% of the energy input from the gas). The electric heaters were turned off for one day (18 September 1995) while burning Illinois #6. By the end of the day, the furnace was too cold for the coal to ignite.

Firing the U furnace with natural gas overnight maintained it at pc conditions. For the week beginning 13 September 1995, the overnight firing rate ranged from 30.8-32.2 kW. After 20 September 1995, the overnight firing rate was decreased to 26.4 kW. Coal firing rates while collecting char varied from 22 kW to 32 kW with most falling in the range of 22-26.4 kW. The coal firing rate on any given day was determined by safety considerations, namely the temperature of the particle-laden combustion gas stream at the inlet of the cyclone. If the entering gases were too hot, unwanted combustion reactions could occur in the cyclone. In order to avoid such reactions, cyclone inlet temperatures were usually maintained below 865 K; in a few instances, inlet temperatures rose to 920 K. The cyclone inlet temperature was a function of the coal firing rate and the quench method used. Hence, if a given quench method did not sufficiently reduce the cyclone inlet temperature, the coal firing rate was decreased so that a safe cyclone inlet temperature was maintained. The 32 kW coal firing rate was used only once- the day the electric heaters were turned off.

Three different quenching systems were used with the char collection system: air injection through the quench gas injector, N₂ injection through the quench gas injector, and air injection through the quench gas injector plus water cooling from the air-atomized water spray nozzle mounted on port 1-1N. When quench air was used alone, control valve setpoints for the air ranged from 560-755 slpm. When quench air was used in conjunction with the water spray nozzle, control valve setpoints ranged from 280-380 slpm while the water flow rate to the nozzle was maintained at 250-300 cc/min. Cyclone inlet temperatures were lowest when both quench air and water spray were used for quenching; temperatures were typically less than 760 K. Finally, when N₂ was used as the quench gas, control valve setpoints were in the range of 235-375 slpm. For comparison, the flue gas flow rate at a coal firing rate of 29.3 kW is approximately 565 slpm.

The stoichiometric ratio in the flame zone was maintained at approximately 1.15 during char collection. This stoichiometry was checked at the beginning of each day by sampling the combustion gases at the furnace exit while burning coal. O₂ concentrations in these daily samples varied between 2.0-3.9% (dry basis). Samples were also withdrawn from port 1-1N at the beginning of each day for the first 2 weeks. O₂ concentrations in these port 1-1 samples varied between 5.0-7.7% (dry basis).

Furnace temperatures were difficult to measure during char collection because the only openings where thermocouples could be inserted into the furnace above port 1-1 were the two-5.25 cm diameter holes where the UV detectors were located. For the first half of the char collection experiments, one UV detector was removed and a thermocouple probe was inserted into the opening. Temperatures were monitored throughout the course of the day from this location 32 cm above port 1-1. At the beginning of the day, measured temperatures were in the range of 1430-1510 K. By the end of a day of char collection,

these temperatures had dropped to 1340-1390 K. Temperatures in port 1-1 were also measured with a thermocouple probe at the beginning of each day while firing coal. These temperatures were in the range of 1500-1600 K. Of course, all these thermocouple probe measurements are probably several hundred Kelvin lower than the actual temperatures as explained in "Temperature Measurement in the U Furnace" on page 174.

B.3 Characterization of Chars

Collected chars were grouped in large plastic buckets by parent coal type, day of collection, and quenching method. For example, if Illinois #6 coal were burned one day and two methods of quenching were used, chars from the two quench methods would be placed in separate buckets. At the end of a day, all newly filled buckets were sealed with lids. After char collection was completed for all coals, the char in each bucket was sifted through a -28 mesh screen (590 μm). The only materials collected on this screen were small pieces of gasket material from the gasket between the steel collection bucket and the cyclone and other pieces of debris. Samples from each of these buckets were then sent to a coal analysis lab on the University of Utah campus. Analyses performed on the samples included % C, % H, % N, and % ash. Approximate percent burnout was computed for each sample based on the carbon and ash content of the parent coal and of the char.

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 the dates of char collection included in that mixture. Examples include Pitt #8 (25,26,29 sept) and K. R. (31 oct, 1 nov).

B.3.1 Chemical Analysis of Chars

Samples from each char mixture were sent to Huffman Laboratories in Golden, Colorado for moisture, ash, calorific value, and ultimate analyses. The complete analyses results for all chars are found in Table B.3 and Table B.4. In addition, Table B.3 contains columns for the computed burnout (based on the carbon and ash content of the parent coal and of the collected char) and the total mass of each char collected. The oxygen content in Table B.4 was determined by difference.

One char listed in both Table B.3 and Table B.4, Nuchar, was obtained commercially from Westvaco Chemicals; a sample was sent to Huffman Laboratories for analysis. Nuchar is an activated carbon made from coconut shells. It is a high surface area (N_2 BET surface area in the range of 1400-1800 m^2/g), high carbon char with an extremely low nitrogen content (0.13% by weight, dry basis).

Nuchar was added to the experimental matrix for several reasons. First, proposed heterogeneous mechanisms for the fate of char-N include the reduction of NO at carbon and nitrogen sites on the char surface. Because Nuchar has a very high carbon content coupled with an extremely low nitrogen content, it may be possible to study the importance of these two competing mechanisms. Second, Nuchar has a very high N_2 surface area

relative to the coal chars (see Section B.3.3), so any NO reduction reactions with carbon on

Table B.3 . Miscellaneous coal char and Nuchar data.

	Moisture (%)	Ash (%)	Calorific Value (kJ/kg)	Computed % Burnout	Total Mass Collected (kg)
Sample Name	as rec'd	as rec'd	as rec'd		
Quench Method = Air					
Pitt #8 (25,26,29 sept)	0.96	35.53	21347	81.6	5.80
Ill #6 (14,19,20,21 sept)	1.01	32.61	22137	85.4	7.73
Ill #6 (18 sept)	0.89	17.85	26633	68.8	2.61
Ill #6 (22 sept)	1.2	27.57	23786	81.3	2.19
Utah (13 sept)	1.27	34.07	21847	78.7	1.09
Quench Method = N ₂					
Pitt #8 (27,28,29 sept)	1.05	26.91	24158	72.9	8.00
Ill #6 (12,13 oct)	0.7	34.89	21167	86.8	1.00
Ill #6 (16 oct)	0.7	27.34	23958	81.1	1.60
K. R. (29,30 oct)	1.13	43.42	17807	83.5	0.76
Black Thunder	0.88	56.17	13862	n/a	0.38
Quench Method = Air + H ₂ O					
Pitt #8 (19,24 oct)	2.89	31.14	22058	77.5	3.70
K. R. (26 oct)	2.77	49.36	15332	86.6	1.20
K. R. (31 oct, 1 nov)	2.05	42.02	17951	82.9	1.15
Commercially-obtained Char					
Nuchar	6.06	5.23	29875	n/a	1.0

the char surface should be enhanced by the amount of available surface area on the Nuchar. Finally, the very low Nuchar nitrogen content contrasts with the much higher nitrogen contents of the coal chars, perhaps allowing for some conclusions to be drawn about the role of char-N.

Table B.4 . Ultimate analyses of coal chars and Nuchar

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
Sample Name	dry	dry	dry	dry	dry
Quench Method = Air					
Pitt #8 (25,26,29 sept)	60.96	0.72	1	0.41	1.04
Ill #6 (14,19,20,21 sept)	65.0	0.52	1.13	0.4	0.05
Ill #6 (18 sept)	75.95	1.21	1.61	0.51	2.71
Ill #6 (22 sept)	70.3	0.56	1.28	0.41	0.05
Utah (13 sept)	65.64	0.71	1.14	0.37	0.05
Quench Method = N ₂					
Pitt #8 (27,28,29 sept)	68.08	0.7	1.14	0.48	2.4
Ill #6 (12,13 oct)	63.03	0.49	1.12	0.46	0.05
Ill #6 (16 oct)	70.65	0.69	1.13	0.51	0.05
K. R. (29,30 oct)	51.23	0.66	0.64	1.62	1.93
Black Thunder	40.12	0.43	0.48	0.62	1.68
Quench Method = Air + H ₂ O					
Pitt #8 (19,24 oct)	65.44	0.48	1.06	0.62	0.33
K. R. (26 oct)	47.31	0.44	0.46	1.58	0.05
K. R. (31 oct, 1 nov)	51.58	0.77	0.51	1.39	2.85
Commercially-obtained Char					
Nuchar	86.48	1.95	0.13	0.02	5.87

All chars were collected in the latter stages of burnout as evidenced by the computed burnouts, which range from 68.8% to 86.8%. In general, the higher the volatile content of the parent coal, the greater the degree of burnout. The degree of burnout is not correlated to the quench method. The char with the lowest burnout level, Ill #6 (18 sept), was collected on the day that the secondary air was not preheated by the electric heaters.

The nitrogen content of the chars (dry basis) ranges from 0.46-1.61%. All chars are nitrogen deficient relative to their parent coals (see Table B.2), indicating that carbon and nitrogen are not released from the coal in parity. This same result was seen when the nitrogen content of the coal samples was measured after completion of the volatiles test (see Table B.2, column “%N after vol.”).

B.3.2 Particle Size Distributions

Particle size distributions for all the chars were determined using the sieve analysis method. In addition, distributions for some of the chars were measured using a Microtrak light scattering analyzer. Both methods are described in Appendix C. Also included in Appendix C are tabulated particle size distributions for all the chars. Some general comments can be made about these distributions. First, based on the sieve analysis method results for the parent coals, only Illinois #6 meets the criteria of 70% by mass through -200 mesh (75 μm), although Knife River comes close. The Utah and Pittsburgh #8 coals are approximately 55% through -200 mesh.

Second, there are large discrepancies between the Microtrak and sieve analysis data with the Microtrak method measuring a much finer particle size distribution than the sieve analysis method. As an example, for Illinois #6 coal, the Microtrak data indicate that 98.7% of the particles by volume (or by mass if constant density is assumed) are smaller than 75 μm while the sieve analysis data show that only 74.4% of the particles by mass are smaller than 75 μm . It seems unlikely that the particle size distribution really is as fine as the Microtrak data indicate since the supplier only guaranteed that 70% of the particles would be smaller than 75 μm . A check of the sieve analysis method was made by comparing particle size distribution data from the Nuchar product literature with the sieve analysis Nuchar results. Product literature states that 95-100% by weight will pass through a sieve size of 150 μm , 85-95% will pass through a sieve size of 75 μm , and 65-85% will pass through a sieve size of 45 μm . In the sieve analysis, 95% by weight passed through a sieve size of 150 μm and 91% passed through a sieve size of 75 μm , in agreement with the product literature. However, only 48% passed through a sieve size of 53 μm . These data suggest that the smaller screen size sieve analysis results could be skewed; distributions below 75 μm may be finer than sieve analysis indicates.

Third, there appears to be no correlation between the particle size distribution of the parent coal, the degree of burnout of the char, and the particle size distribution of the char. Nevertheless, in general the char particle size distributions are slightly coarser than those of the parent coals.

B.3.3 N₂ BET Surface Area and Porosity Analysis

The N₂ BET technique characterizes the mesopore and some of the micropore structure of the char (pores with radii in the range of 1.5-50 nm). Since it has been proposed that the heterogeneous reactions of char-N and NO_x occur predominantly in the mesopores, knowledge of the surface area and porosity of the chars could be useful in the

analysis of the data. Hence, N₂ BET surface area and porosity measurements were run on a select group of chars by a University of Utah laboratory; the laboratory did not correct the porosity data for large surface pores. All the data are listed in Table B.5. The fact that the measured Nuchar surface area falls within the manufacturer's specifications (1400-1800 m²/g) is an indication that the coal char results are valid.

Table B.5 . Surface area and porosity for selected chars.

	N ₂ BET Surface Area	N ₂ BET Porosity
Sample Name	(m ² /g)	(cc/g)
Pitt (25,26,29 sept)	23.8	0.02
Pitt (27,28,29 sept)	52.1	0.05
Utah (13 sept)	51.4	0.06
Ill (14,19,20,21 sept)	57.6	0.03
Ill (16 oct)	71.5	0.07
Ill (18 sept)	104.8	0.11
K. R. (31 oct, 1 nov)	43.2	0.08
Black Thunder	66.3	0.08
Nuchar	1678	1.44

These data can also be compared to similar data collected by White et al. (1991) for coal chars prepared at high heating rates in a flat flame burner (maximum temperature of 1473 K). A char sample prepared from Pittsburgh #8 coal had a measured N₂ BET surface area of 74.6 m²/g and a porosity of 0.056 cc/g. For char samples prepared from other coals, the surface areas ranged from 47-313 m²/g and porosities ranged from 0.024-0.164 cc/g. The data presented in Table B.5 are in the same range as the data reported by these researchers.

Based on the data in Table B.5, the N₂ BET surface area of Nuchar exceeds that of the coal chars by more than an order of magnitude. This huge difference has implications for the interpretation of experimental results in this report. N₂ BET surface area is not correlated to the level of burnout, although the char with the highest measured surface area, Ill (18 sept), is the char that is least burned out.

B.3.4 SEM Analysis

Samples of three chars were further analyzed with a scanning electron microscope (SEM): Ill (18 sept), K. R. (31 oct, 1 nov), and Nuchar. Detailed photographs of each of the three chars taken at two levels of magnification can be found in Chapter 4 of Spinti (1997). The contrasts between the three chars are striking. One obvious contrast is that of particle size distribution. The Nuchar sample has a fine, fairly uniform particle size distribution. The Ill (18 sept) char sample has much bigger particles and a wider particle size distribution than the Nuchar. Lastly, the K. R. (31 oct, 1 nov) char sample has almost a bimodal particle size distribution centered around (1) particles similar in size to the bigger particles of the Ill (18 sept) char sample and (2) material that is finer than particles in the Nuchar sample. These visual observations correlate well with the sieve method particle size distributions in Appendix C of Spinti (1998). For example, while 91.0% of the Nuchar sample passed through the 75 μm sieve, only 67.2% of the Ill (18 sept) sample and 43.3% of the K. R. (31 oct, 1 nov) sample passed through the same sieve. Also, 90.5% of the Ill (18 sept) sample passed through the 150 μm sieve compared to 80.2% of the K. R. (31 oct, 1 nov) sample, so a larger fraction of the Knife River char is made up of particles bigger than 150 μm .

Another contrast noted in the SEM analysis relates to particle shape, density, and texture. The Nuchar particles are angular in shape and appear to be very dense. There are no obvious holes in the char structure. The Ill (18 sept) char particles have more rounded shapes and a variety of textures and densities. There are lacy-type structures which are probably the ash matrices of burned out char particles. Other particles are very porous in appearance with many visible openings in the particle structure, similar to a sponge. Still other particles appear very dense with relatively smooth surfaces and only a few visible openings. Finally, there are some cenospheres, which are formed when ash (i.e., mineral matter) undergoes surface melting followed by expansion to a spherical shape. The very fine material which is plentiful in the K. R. (31 oct, 1 nov) char appears to be cenospheres. The large particles have rough textures and appear to be highly porous.

An important conclusion can be drawn based on the SEM analyses: neither of the coal chars is homogeneous in composition. Particles at all stages of burnout can be found, from highly burned out ash structures to very dense-looking particles with few openings that probably have a high carbon content. In contrast, Nuchar has a fairly homogeneous composition based on the appearance of the particles in the SEMs.

C. Appendix C - Experimental Methods

This appendix outlines the basic protocols and methods that were used for all experiments with both simulated coals and the actual parent coals.

C.1 Description of Experimental Methods

C.1.1 Protocol for Typical Experiment with Simulated Coal

In these experiments, furnace inputs that could be varied included the gas and char firing rates, the stoichiometric ratio, the type of oxidant, gas phase NO_x concentration, and furnace temperature. As explained on page 26, the gas and char firing rates were set at 24.9 kW and 4.4 kW respectively except for tests involving firing rate. The stoichiometric ratio was set at 1.15 (approximately 3% excess O₂) unless the effect of O₂ concentration was the test parameter. The oxidant of choice for most experiments was air due to the cost and difficulty of running the artificial system. The gas phase NO_x concentration varied according to the experiment. If artificially high NO_x levels were required, either NH₃ or NO, metered by a MFC, was injected into the natural gas line. The MFC was then adjusted until the measured gas phase NO_x concentration reached the desired level as described in “NH₃ and NO Addition” on page 171. With air as the oxidant, furnace temperature could be altered by changing the setpoint on the electric heaters used to preheat the secondary combustion air or by turning them off altogether. In most cases, the heaters were on at a setpoint of 590 K.

Thus, the “typical” simulated coal experiment was conducted in preheated combustion air at 3% excess O₂ with or without addition of NH₃ or NO. Under these conditions, temperatures measured in the mixing chamber of the premixed burner ranged from 490-530 K. Temperatures measured by a thermocouple inserted through the window in Section 7 near the furnace exit ranged from 815-875 K. At these combustor conditions, char burnout as measured by excess O₂ concentration was nearly complete by port 1-1, the location closest to the burner from which samples could be withdrawn. Based on excess O₂ concentrations measured in the furnace exhaust (i.e., port 6-4), char burnout levels exceeded 99% during most of the simulated coal experiments.

Pressures in the U furnace were maintained near local atmospheric pressure for all experiments. A pressure tap located at port 4-1E was used for monitoring purposes. A damper located at the entrance to the laboratory flue was adjusted until the port 4-1E pressure tap measured 0 kPa (gauge). Pressures upstream of port 4-1 reached approximately +0.06 kPa (gauge) while pressures downstream of port 4-1 reached -0.06 kPa (gauge).

Furnace operating conditions for experiments conducted in Ar/CO₂/O₂ were similar to those described above with one exception. Furnace temperatures dropped slightly due to the heat losses that occurred during the time it took to shut the air system down and get the

artificial oxidant system running. Protocols established for the use of the Ar/CO₂/O₂ system are detailed on page 166.

Two sampling locations were utilized for all simulated coal and parent coal experiments. One location was port 1-1N, the port closest to the burner. This port is located approximately 30 cm below the bottom of the quartz. The other location is port 6-4W. Samples pulled from this port are referred to as exhaust samples because port 6-4 is the last port in the furnace.

At each experimental condition, the gas sample was first analyzed by the control room instruments (CO/CO₂ analyzer, O₂ analyzer, chemiluminescent NO_x analyzer) before being sent to the FT-IR. This order was chosen based on the response time of the control room instruments versus that of the FT-IR. The FT-IR response time to any changes and/or fluctuations is slow and the fluctuations are damped because of the large volume of the FT-IR cell (2.3 l). In contrast, the response time of the control room instruments is determined only by the residence time of the sample in the sample line. Thus, the control room instruments were used to monitor gas phase composition changes which occurred after any furnace input was altered. Once these instruments indicated that the furnace had stabilized at the new settings, the control room instrument data were logged for 3 min. After logging, the sample flow was switched to the FT-IR and the FT-IR spectrum was taken.

Temperature measurements in the simulated coal experiments were made using a suction pyrometer and fine wire thermocouple probes. For details on the protocols used for temperature measurement, see "Temperature Measurement in the U Furnace" on page 174.

C.1.2 Estimating Contributions of Char-N and Other NO_x Sources to Total NO_x Measured

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 additional gas phase NO_x that is produced when char is added to the system. For the first half of the char experiments, the following method was used to obtain these data points. First, natural gas was fired at 29.4 kW and a desired stoichiometric ratio (1.15 for example), and the NO_x concentration was recorded. Next, the combustion air flow rate was increased in order to maintain the desired stoichiometric ratio (1.15) after char addition, and char was fed to the system. The NO_x concentration resulting from this gas/char flame was recorded. The contribution of char-N to the total NO_x concentration was assumed to be the difference between the NO_x associated with the gas flame and the NO_x concentration measured in the gas/char flame. To obtain a value for the NO_x associated with the gas flame, the NO_x concentration measured when firing natural gas was diluted by the increased combustion air flow rate required for burning the gas/char mixture. This approach has been termed the "constant excess air" or CEA method.

However, upon consideration of the time scales of combustion for natural gas and char, the author concluded that this method of estimating the portion of the total NO_x associated

with the gas flame during the combined gas/char firing was incorrect. The time scale of combustion for a premixed natural gas flame is on the order of milliseconds while the time scale for char oxidation is on the order of several hundred milliseconds or even longer. Extrapolating this information to the gas/char flame, the two fuels burn sequentially. The natural gas burns first in an O₂ environment that is essentially unused by the char. Hence, the O₂ concentration in the gas phase at the end of natural gas combustion and prior to char oxidation will be much higher than 3%. Based on this theory of sequential burning, the correct method for estimating the NO_x associated with the gas flame is to fire the natural gas alone with the combustion air required for the gas/char flame at the desired stoichiometric ratio and then to measure the NO_x concentration. This approach has been termed the “constant flow rate” or CFR method.

An important question to ask is how different is the NO_x contribution estimated from the two methods? In a typical case, the NO_x concentration for the CEA method was 224 ppm, which the dilution correction reduces to 187 ppm. In contrast, the CFR method NO_x concentration was 138 ppm. Clearly, these two methods are not equivalent because of the dependence of NO_x formed in a natural gas flame on excess air. The author felt the CFR method was a more correct way to interpret the data, so all data collected using the CEA method were corrected to the CFR method using appropriate correction curves. Details of how these corrections were made are given in Appendix E.

Figure C.1 shows a comparison of FT-IR data from the two methods (CEA and CFR) taken during the second half of the char-N experiments. NO_x concentration in the exhaust is reported as a function of excess O₂. Although the CFR method was used for data interpretation, both CEA and CFR data points were logged at each experimental condition for comparison purposes. Because the CFR data were taken with enough combustion air to oxidize both the natural gas and the char at the desired stoichiometric ratio, measured O₂ concentrations are higher and NO_x concentrations are lower than the corresponding CEA data. Also included in Figure C.1 are all CEA data taken prior to the introduction of the CFR method. Note how consistent the three sets of data are relative to each other.

C.1.3 Protocol for Typical Experiment with a Parent Coal

The “typical” experiment with a parent coal was very similar to the “typical experiment” with a simulated coal; it was conducted in preheated combustion air (electric heater setpoint = 590 K) and the target firing rate was 29.3 kW. Excess O₂ levels were varied to ascertain the effect of excess O₂ on NO_x formation from coal. A few tests were also conducted in Ar/CO₂/O₂ for comparison with the simulated coal results. As with the simulated coal, sampling locations were ports 1-1N and 6-4W and sampling order was the control room instruments first and the FT-IR second.

C.2 Computation of Char-N to NO_x Conversion

The y-axis for much of the data plotted in this appendix and in much of this report reads either “% Conversion of Char-N to NO_x” or “Actual % Conversion of Char-N to NO_x.”

Understanding how these conversions were computed is critical to understanding the interpretation of the data.

“% Conversion of Char-N to NO_x” is only used on plots of experiments which were run in artificial oxidant with no NH₃ or NO doping. In these experiments, there were only two sources of nitrogen in the system- the nitrogen in the char and a small amount of nitrogen in the natural gas (typically around 3% by volume). Compensation for the small amount of nitrogen in the natural gas was made by measuring the NO_x level in a natural gas/artificial oxidant flame and then subtracting that NO_x concentration from all NO_x measurements made when burning simulated coal in artificial oxidant. NO_x emissions from a natural gas/artificial oxidant flame were measured on two separate occasions; resulting NO_x concentrations were 17 ppm and 18 ppm, so 17 ppm was chosen as the value to subtract. After compensating for NO_x production from the nitrogen in the natural gas, the only possible source of NO_x is the char-N, so measured NO_x concentrations represent the actual conversion of char-N to NO_x.

The percent conversion of char-N to NO_x is computed according to the following formula.

$$Conversion = \frac{((NO_{x, meas} - 17)/10^6) \times Q_{dry} \times MV}{F_{dry} \times N_{dry} \times MW_N} \quad (3)$$

Figure C.1 . Comparison of NO_x concentrations measured by the FT-IR using the CEA and CFR methods. Natural gas firing rate is 24.9 kW. Sampling location is port 6-4W.

where

Conversion = Actual percent conversion of char-N to NO_x

NO_{x,meas} = NO_x measured in simulated coal/artificial oxidant experiment

Q_{dry} = Total dry furnace flow rate for the simulated coal; calculated on U furnace spreadsheet based on furnace inputs

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.

In plots of all other experiments, the y-axis is labeled as “Apparent % Conversion of Char-N to NO_x.” Conversion is apparent and not actual because in such experiments there are other NO_x sources including thermal NO_x and NO_x resulting from NH₃ or NO doping. The apparent conversion is based on the incremental change in measured NO_x that results when char is added to a natural gas flame. As shown in subsequent plots, that incremental change can be either positive or negative.

The apparent percent conversion of char-N to NO_x is computed according to equation (4).

$$Conversion = \frac{((NO_{x, gas + char} - NO_{x, CFR}) / 10^6) \times Q_{dry} \times MV}{F_{dry} \times N_{dry} \times MW_N} \quad (4)$$

where

NO_{x,gas+char} = NO_x measured with simulated coal

NO_{x,CFR} = NO_x measured with corresponding CFR data point

and all other variables are as defined for equation (3).

Errors in computing percent conversion can result from errors in any of the following inputs to the conversion equation: char feed rate, dry furnace flow rate, actual nitrogen content of the char, and measured NO_x concentration. The char feed rate error is small because the Ktron feeder was calibrated for each char. The measured NO_x concentration error is also small because almost all NO_x measurements were confirmed by two different instruments- the chemiluminescent NO_x analyzer and the FT-IR. The error in nitrogen content of the char is dependent on whether or not the sample sent to the lab was representative of the whole char. Each char was thoroughly mixed in a sealed bucket prior to sampling, so this error was

minimized. Finally, the dry furnace flow rate error depends on the accuracy of the calibrations of the rotameters, control valves, and feeder that supply the fuel and oxidant streams to the furnace. Based on calibration data for these rotameters, control valves, and feeder, the error in computed dry furnace flow rates is estimated to be less than 5% with air as the oxidant and less than 10% with Ar/CO₂/O₂ as the oxidant.

C.3 Consistency of Baseline Data

U furnace firing conditions were very consistent throughout the course of the char-N and parent coal experiments. This consistency is seen in Figure C.2, which is a plot of “gas baseline” data from the period when char-N and parent coal experiments were conducted. “Gas baseline” refers to the following firing conditions: the fuel is natural gas, the firing rate is 29.3 kW, the stoichiometric ratio is 1.15, and the electric heaters are on (setpoint = 590 K). As noted previously, the FT-IR NO_x measurements are slightly higher than the chemiluminescent NO_x analyzer (TECO) NO_x measurements. Most of the measured FT-IR NO_x levels fall in a narrow band between 230-270 ppm.

Natural gas NO_x data taken at various concentrations of excess O₂ were seen in Figure C.1. These data were also taken over a period of several months. The repeatability of the data over this length of time is excellent. Figure C.3 is a plot similar to Figure C.1 (i. e. the same type of FT-IR data were taken over the same time period) except that the data are from port 1-1N. The data labeled CEA and CFR were logged in pairs at each experimental condition during the second half of the char-N experiments; the data labeled CEA (prior to CFR) were taken prior to the introduction of the CFR method. Due to differences between the two methods, CFR O₂ concentrations are higher and NO_x concentrations are lower than the corresponding CEA concentrations. As with the data in Figure C.1, the repeatability of this data is very good. A final check of the consistency and repeatability of data obtained from the U furnace is seen in Figure C.4.

Data for this plot were taken at various gas phase NO_x levels from port 6-4W; the data points clustered around 500 ppm and 900 ppm were obtained with NH₃ and NO doping. The data on this plot were acquired during the second half of the char-N experiments when both CFR and CEA data were collected; data are plotted as CFR NO_x versus CEA NO_x. Two straight lines are fit to the data, one line for the FT-IR data and one line for the TECO data. The R² for both lines is greater than 0.998, indicating the consistency of the data set. These two lines were used to correct CEA data taken during the first half of the char-N experiments to CFR data as explained in Appendix E.

C.4 Effect of Chosen Operating Conditions

As mentioned previously, protocols were established for the production of chars and for the subsequent firing of simulated coal. The effects of the more important protocols will be discussed next. Unless otherwise indicated, all data were taken from port 6-4W and the overall stoichiometric ratio in the gas/char flame was 1.15 (approximately 3% excess O₂).

Figure C.2 . Natural gas baseline NO_x data taken over the period of char-N testing. Gas firing rate is 29.3 kW.

Figure C.3 . Repeatability of NO_x concentrations obtained with the CEA and CFR methods. Natural gas firing rate is 24.9 kW. Sampling location is port 1-1N.

To begin, for most experiments the firing rates of natural gas and char were 24.9 kW and 4.4 kW respectively in the simulated coal. However, the effect of relative firing rates of natural gas and of char needs to be considered. In an experiment performed with Ill (14,19,20,21 sept) char, the char firing rate was held constant at 4.4 kW while the natural gas firing rate was varied. The results of this experiment are found in Figure C.5. The apparent conversion of char-N to NO_x is plotted versus the percent of the total energy input that comes from the char. Over the range of natural gas firing rates tested (20.2-33.3 kW), the apparent conversion is relatively unchanged. Similar results were obtained with Pitt (27,28,29 sept) char.

The data in Figure C.6 were collected by holding the natural gas firing rate constant at 24.9 kW and varying the char firing rate; Pitt (25,26,29 sept) char and Ill (18 sept) char were tested. The results are plotted as apparent conversion of char-N to NO_x versus the ratio of the char firing rate to the gas firing rate. As in Figure C.5, over the range of char firing rates tested (2.05-8.8 kW), there is little change in apparent conversion. Additional data relating to the issue of char firing rate was presented in Section 3.0. Clearly, these two figures indicate that the chosen firing rates of natural gas and char did not significantly affect the outcome of the experiments.

Another protocol for the simulated coal experiments was that the char was premixed with the natural gas and combustion air in the burner. To check whether or not char injection location affected char-N to NO_x conversion, an experiment was run where a Utah char was injected into the furnace through port 1-2. The same char was also injected through the burner. Computed

char-N to NO_x conversions for the two different injection locations were within 2% of each other, so char injection through the burner was considered to be satisfactory.

Another protocol of concern was the method of quenching employed during the char production phase of the experiments. Three quench methods were used: quenching with air, quenching with N₂, and quenching with air plus water spray. All three quench methods were used in collecting Pittsburgh #8 char. The Pitt (25,26,29 sept) char, quenched with air, had a carbon burnout level of 81.6% and a nitrogen content by weight (dry) of 1.0%. The Pitt (27,28,29 sept) char, quenched with N₂, had a carbon burnout level of 73.0% and a nitrogen content by weight (dry) of 1.14%. The third Pitt char, Pitt (19,24 oct), quenched with air plus water spray, had a carbon burnout level of 77.5% and a weight percent nitrogen (dry) of 1.06%. Hence, carbon burnout levels in the chars varied slightly while nitrogen contents (dry basis) were about the same.

Data from all three chars are plotted in Figure C.7. The data were collected at typical low-NO_x firing conditions, i.e., the flame was doped with NH₃ or NO such that gas phase NO_x levels prior to the addition of char were 430-450 ppm. Conversions of char-N to NO_x at these conditions vary only 4% between the three chars. Based on these results, the quench method is probably not of much concern in the analysis of the char-N experiments. Of greater concern may be the effect of char carbon content, ash content, nitrogen content, and/or internal surface area, all of which depend on the extent of char oxidation in the parent coal prior to quenching.

Figure C.4 . Consistency of CFR versus CEA data over a range of NO_x concentrations. Gas firing rate is 24.9 kW. Measured excess O₂ for the CEA method is approximately 3%.

Figure C.5 . Effect of varying the natural gas firing rate during a simulated coal experiment with Ill (18 sept) char. Char firing rate is 4.4 kW.

The final protocol issue to be addressed is that of using NO and NH₃ interchangeably to dope the simulated coal flames. Clearly, NH₃ should not be used for doping if NH₃-doped flames produce different results than NO-doped flames. Two chars, Pitt (27,28,29 sept) and Ill (22 sept), were tested in simulated coal flames doped with NH₃ and then with NO. Test results are plotted in Figure C.8 as apparent conversion of char-N to NO_x versus "Initial NO_x". The "Initial NO_x" label refers to the exhaust NO_x concentration measured by the CFR method prior to the addition of char. The scatter in the data appears to be as great as any differences between the NH₃ and NO data points. The trends are exactly the same with both gases. This result is not unexpected since NH₃ reactions occur on much faster time scales in the simulated coal flame than the char reactions. Consequently, results obtained with both NH₃ and NO will be used interchangeably in the rest of this report.

Figure C.6 . Effect of varying the char firing rate during simulated coal experiments.
Natural gas firing rate is 24.9 kW.

Figure C.7 . Comparison of conversion results from Pittsburgh #8 coal chars quenched by three different methods. The natural gas firing rate is 24.9 kW; the char firing rate is 4.4 kW.

Figure C.8 . Comparison of NO versus NH₃ doping results from simulated coal flames.