gas phase reactions did not play a significant role in the reduction of gas phase NO_x that was produced initially.

3.2 Polycyclic Aromatic Hydrocarbons

3.2.1 Introduction

The Clean Air Act Amendments (CAAA) of 1990 contain provisions which will set standards for the allowable emissions of 188 analytes designated as hazardous air pollutants (HAPs). This list of HAPs was used to establish an initial list of source categories for which EPA would be required to establish technology-based emission standards, which would result in regulated sources sharply reducing routine emissions of toxic air pollutants. Polycyclic organic matter (POM) has also been referred to as polynuclear or polycyclic aromatic compounds (PACs). Nine major categories of POM have been defined by the EPA (Brooks, 1989). The study of organic compounds from coal combustion is complex and the results obtained so far are inconclusive with respect to emission factors (Curtis et al., 1993). The most common organic compounds in the flue gas of coal-fired power plants are polycyclic aromatic hydrocarbons (PAHs). Furthermore, EPA has specified 16 PAH compounds as priority pollutants. These are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, and dibenz[ah]anthracene.

3.2.2 Objectives

The objectives of this portion of the study were to measure the emissions of PAHs from a laminar flow, bench-scale drop-tube reactor and from Penn State's demonstration-scale facility. The effects of temperature and oxygen concentrations on the formation and destruction of PAHs were studied. Monitoring was limited to the 16 EPA-specified priority hazardous pollutants. Results from similar studies undertaken in Penn State's pilot-scale research boiler, down-fired combustor, and bench-scale reactor were reported in the Phase II final report (Miller et al., 2000) and elsewhere (Pisupati et al., 2000).

3.2.3 Description of Equipment and Experimental Matrix

3.2.3.1 Drop-Tube Reactor

The electrically-heated drop-tube reactor (DTR) can simulate the heating rate, temperature profile and particle residence time of a utility boiler. The DTR has an alumina muffle tube, which is 6.35 cm in internal diameter and 95.25 cm long, with a maximum temperature (1,550° C) zone of 50.8 cm. Coal is delivered vertically into the reactor. Selected operating temperatures for this study were between 800° C and 1,400° C. A coal feed rate of 0.33 ± 0.01 g/min and a primary air flow rate (to entrain the coal into the reactor) of 1.0 ± 0.1 l/min were used. An additional 3.0 ± 0.2 l/min of secondary air preheated to 250° C was introduced making the total combustion air flow 4.0 ± 0.2 l/min, which corresponds to an air to fuel ratio of approximately 1.25/1 for the selected coal feed rate. A second series of tests was conducted at the same coal feed rates and temperatures with the combustion air reduced to produce an air to fuel ratio of approximately 1/1. Residence time for individual particles in the DTR was approximately one second. The DTR is shown schematically in Figure 3.2.1.

3.2.3.2 Demonstration Boiler

Penn State operates a 15,000 lb steam/h boiler system in which demonstrations of coal-based fuels fired in industrial boilers are conducted, hardware development is performed, and emissions characterization and their control are tested. The boiler is a D-type design watertube boiler manufactured by Tampella Power Corporation, rated for 15,000 lb/h saturated steam (@300 psig), and integrated into the University's steam distribution system. The boiler was designed to fire fuel oil but the overall system has been modified to fire coal-based fuels (i.e., coal-water slurry fuel (CWSF) and dry, micronized coal). Modifications were made to the original system to provide combustion air and CWSF preheating, fly ash removal from the flue gas using either a conventional fabric filter baghouse or a ceramic filter system, coal unloading, storage, and crushing, and either CWSF preparation or dry coal micronization. Figure 3.2.2 shows the micronized coal-fired boiler system with both the pulse-jet baghouse and ceramic membrane filter chamber. The on-line coal handling and processing equipment is shown in Figure 3.2.3 and described in detail in the Phase II final report (Miller, et al., 2000)

The system is located in two buildings at University Park's East Campus Steam Plant except for the baghouse and ceramic filter chamber, which are located outdoors. The boiler and

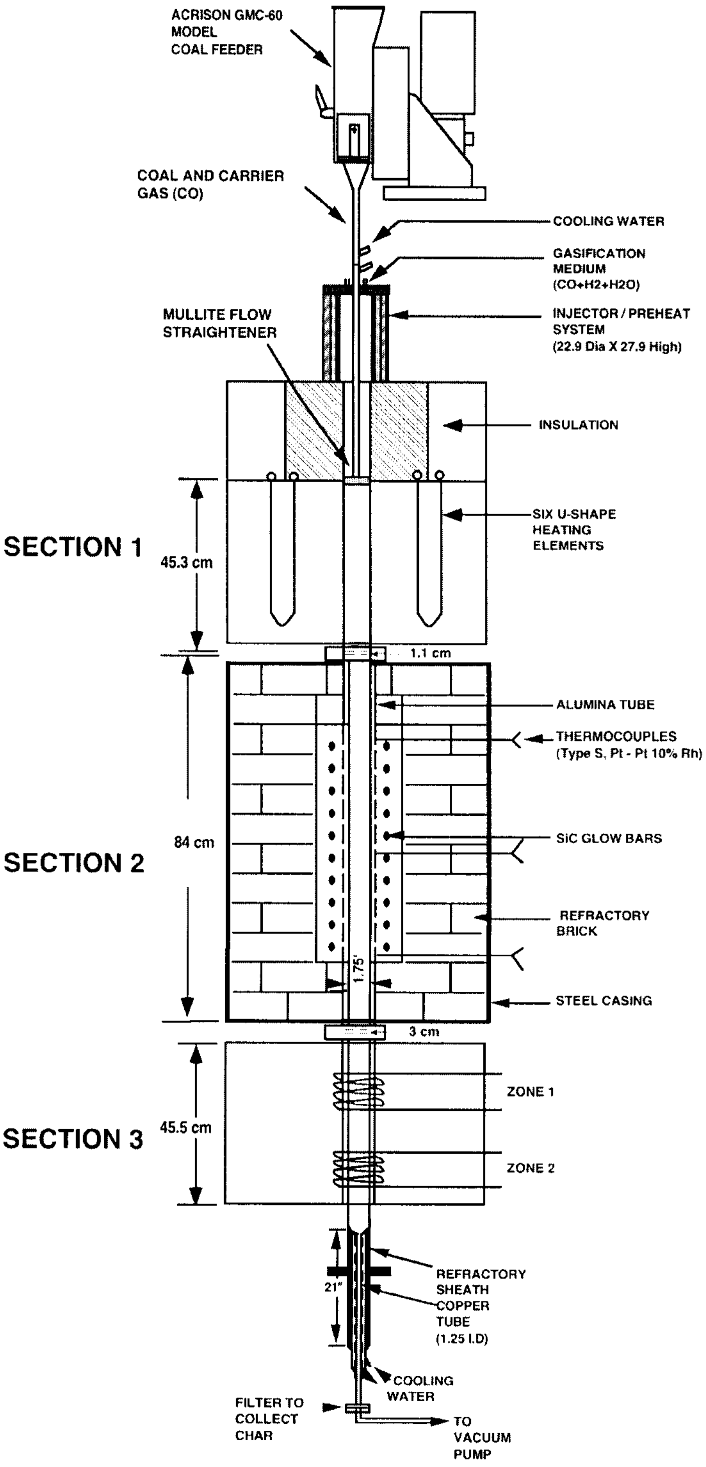

Figure 3.2.1 SCHEMATIC DIAGRAM OF THE DROP-TUBE REACTOR

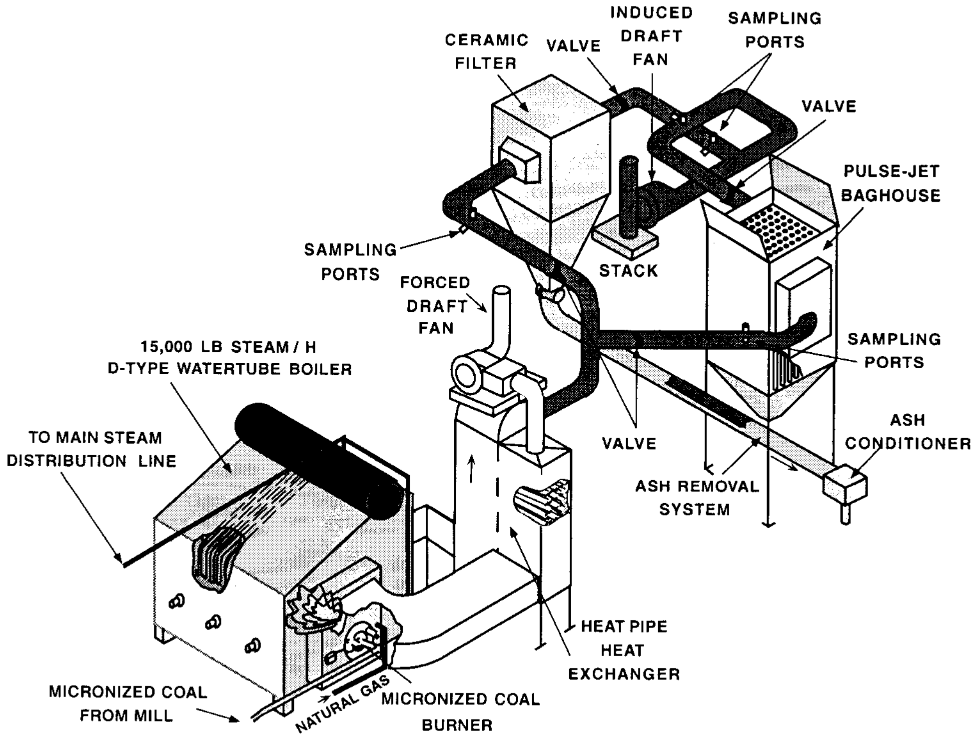

Figure 3.2.2 **GENERALIZED DIAGRAM OF PENN STATE'S MICRONIZED COAL-FIRED DEMONSTRATION BOILER SYSTEM WITH A CERAMIC MEMBRANE FILTER CHAMBER AND PULSE-JET BAGHOUSE**

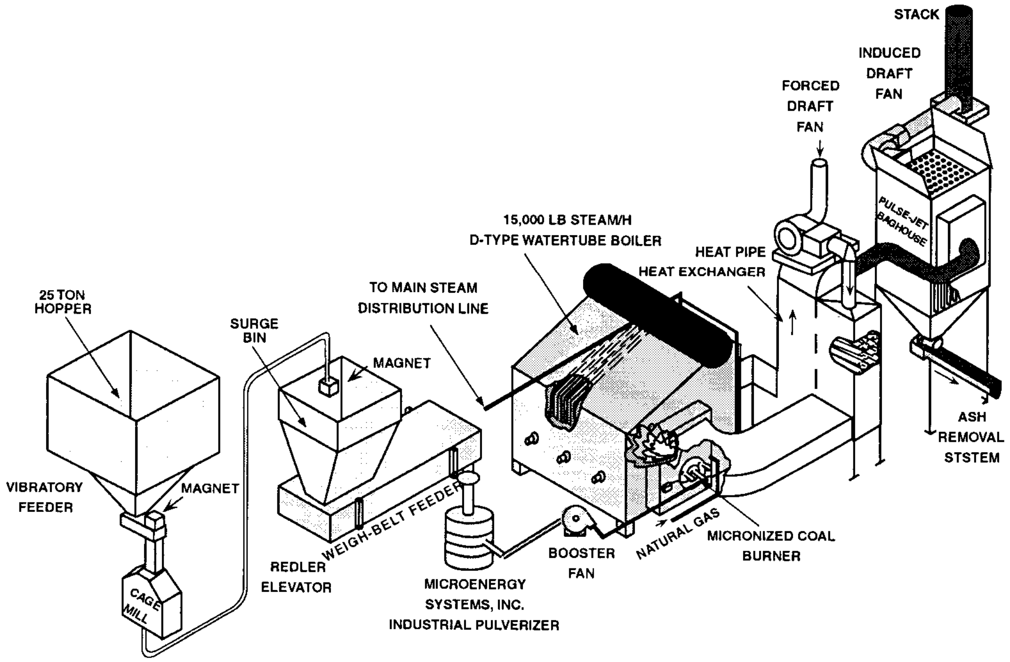

Figure 3.2.3 **GENERALIZED DIAGRAM OF PENN STATE'S MICRONIZED COAL-FIRED DEMONSTRATION BOILER SYSTEM WITH A PULSE-JET BAGHOUSE**

heat pipe heat exchanger are located in the boilerhouse, which is adjacent to Penn State's East Campus Steam Plant. The coal processing and handling equipment is located in the Fuel Preparation Facility and includes a 25-ton coal hopper, a cage mill, several magnets, a Redler conveyor, a 3-ton surge bin, a weigh-belt feeder, a MicroEnergy Systems, Inc. (TCS) industrial mill, and a booster fan to pneumatically transport the coal approximately 150 feet from the booster fan to the burner front in a four inch schedule 40 pipe contained in an underground trench.

The boiler's combustion chamber and convective pass have not been modified specifically for coal firing except that several ports were installed for flame observation and sampling. The furnace is approximately 8 ft long by 6 ft wide, with a volume of $370ft^3$. The bulk gas residence time in the furnace is less than one second. The boiler contains 1,730 ft^2 of effective heating surface.

Four sets of operating conditions involving changes in excess oxygen and fuel firing rate were studied. Tests performed at 5.2% excess oxygen were termed 'High-Air' (HA). Tests performed at 3.7% excess oxygen were termed 'Low-Air' (LA). Tests performed at 14.5 million (MM) Btu/h feed rate were termed 'High-Fire' (HF). Tests performed at 11.0 MM Btu/h feed rate were termed 'Low-Fire' (LF). The four sets of tests were conducted by varying these parameters. For each test, flue gas samples were simultaneously collected from sampling ports located both upstream and downstream of the cloth filter baghouse. All other parameters involving routine operation of the demonstration boiler were held constant and standard boiler operating procedures were followed.

3.2.3.3 Fuel Analysis

The fuel used for these studies was a Middle Kittanning seam coal micronized to ≈80% passing US Standard 325 mesh (commonly referred to as a micronized coal, or "MC grind"). Tables 3.2.1 and 3.2.2 show the analysis of the Middle Kittanning feedstock coal.

3.2.4 Analytical Methodology

A majority of the analytes listed in the CAAA, including PAHs, can be collected by what is commonly referred to as a Modified Method 5 (MM5) sampling train. The train is used to

Table 3.2.1 Proximate Analysis and Higher Heating Value

Sample	% Moisture (Air Dried)	% Ash (Dry)	% V.M. (Dry)	% Fixed C (Dry)	HHV(Btu/lb) (Dry)
Middle Kittanning	0.80	5.24	30.72	64.04	14,350

Table 3.2.2 Ultimate Analysis

Sample	% Carbon (Dry)	% Hydrogen (Dry)	% Nitrogen (Dry)	% Sulfur (Dry)	% Oxygen (Dry)
Middle Kittanning	80.41	4.84	1.41	0.72	7.51

isokinetically collect samples at desired locations in flue gas streams. The collected sample can be separated into solid, condensed liquid and gaseous phases. The PAHs of interest are extracted from the collected sample, concentrated, then separated and quantified by gas chromatography/mass spectrometry (GC/MS).

A modular sampling train meeting all of the requirements of EPA Methods 5 and 0010 was utilized for sampling. EPA Methods 1 through 4 were utilized to determine various parameters needed for isokinetic sampling of the DTR. EPA Method 8270-C was selected for determining the concentrations of PAHs in the collected samples. Extraction of PAHs from the collected particulate matter and the XAD-2 polymeric resin fractions was done by EPA Method 3540-C, Soxhlet Extraction. Extraction of PAHs from the collected liquid fraction was done by EPA Method 3510-C, Separatory Funnel Liquid-Liquid Extraction. Sample cleanup was accomplished by EPA Method 3630-C, Silica Gel Cleanup.

The EPA Method 5 sampling train is designed to isokinetically sample a flue gas stream. A portion of the gas stream was withdrawn from the bottom of the DTR through a heated probe where the particulate matter was filtered out of the stream. The remaining portion of the gas stream was passed through a condenser, a module containing the polymeric resin, and a series of glass impingers immersed in ice water where the remaining condensable analytes were collected.

Specifically, the sampling train contained the following components. They are listed from the most upstream component to the most downstream component.

A straight stainless steel nozzle is located at the end of a sampling probe. The nozzle opening is placed into the flue gas stream facing upstream with pitch and yaw angles of 0°. The inside diameter of the nozzle is precisely known, as its size affects the sampling rate.

Connected to the nozzle by a Teflon® ferrule is a probe of borosilicate glass surrounded by a stainless steel jacket. The tip of the nozzle was introduced 5 cm into the bottom of the DTR. The stainless steel jacket contains heating elements. While sampling, the probe was maintained at 250°F by a temperature controller. The seal between the DTR/probe interface was made airtight from the surroundings using insulation.

The probe was connected to a borosilicate glass filter assembly located within a heated oven. The filter assembly was also maintained at 250°F. A filtering media was selected to retain particles larger than 0.2 μm.

Gases exiting the filter assembly were passed through a water-cooled glass condenser to condense PAHs that may be in the vapor phase. This condensate and remaining gas phase components were passed over the water-cooled porous polymeric resin contained in a glass module.

Gases and condensed liquids were passed through the glass resin module into a chilled condensate knockout trap. This trap was similar in design to an empty impinger. Many analytes not retained on the resin were collected in this knockout impinger.

The next three downstream chilled impingers were used to collect additional water condensate. The final impinger contained indicating-type silica gel to protect the pump from unwanted moisture. The temperature of the gas stream exiting this final impinger was maintained at or below 68°F. All glass ball-and-socket connections were clamped and made airtight with Teflon® O-rings.

The gases were passed through an air tight pump, dry gas meter, across a manometer, (gas samples may be collected at this point if desired) and vented. These devices, along with thermocouple readouts, temperature controllers, manometers, valves, timer and other equipment were contained in a metering console.

3.2.5 Operation of the MM5 Sampling Train

Prior to sampling, data sheets were prepared and leak checks were performed on the sampling system. Proper temperatures and flow rates were maintained. Leak checks were also performed at the conclusion of the sampling runs. All other appropriate EPA sampling procedures were adhered to, and all samples were collected within the acceptable sampling range of 90 to 110% of isokineticity.

3.2.6 Sample Recovery and Preparation for Analysis

The collected sample can be separated into six (or more) fractions. The subsamples contained materials collected from these particular sections of the sampling train. Typically, the first subsample contained recovered materials from the nozzle to the filter assembly. The second subsample contained the filtering media, filtered solids, and other solids removed from the filter assembly. The third subsample contained recovered materials from the back half of the filter paper assembly and the condenser. The fourth subsample contained recovered materials from the resin module. The fifth subsample contained recovered materials from the condensate knockout trap. The sixth and final subsample contained recovered materials from the silica gel-filled impinger. These six subsamples can be processed and analyzed separately or combined in any manner and analyzed. Five of the six subsamples were combined into two samples in the following manner.

The first of the two samples was generated using the following procedure. The recovered particulate matter from the front half rinse and the recovered particulate matter from the filter and the filter itself were spiked with a known amount of a surrogate spiking solution and transferred into a glass soxhlet extraction thimble. The surrogate compounds are compounds chemically similar to the analytes of interest, but not expected to be contained in the extract. The surrogate compounds were utilized to monitor unusual matrix effects or sample processing errors during the extraction and recovery process. The glass thimble was placed into a soxhlet extractor and connected to a round bottom flask containing approximately 10 clean Teflon® boiling chips and enough methylene chloride to maintain extraction cycling. A bulb type condenser was connected atop the extractor. A heating mantle was placed under the flask and adjusted to cycle the extractor about once every thirty minutes for approximately 18 hours.

The remaining front half rinse was quantitatively transferred to a separatory funnel, and serially extracted three times with methylene chloride. The pH of the rinse was then adjusted to at least 11 with sodium hydroxide and serially extracted three more times. The pH was then adjusted to below 2 using sulfuric acid and serially extracted three additional times. This extract was combined with the soxhlet extracted material. A Kuderna-Danish (K-D) concentrator was assembled by attaching a 10 ml concentrator tube with Teflon ® boiling chips to a 500 ml evaporatory flask. The extracts were passed through a sodium sulfate filter to remove any residual water and transferred into the concentrator. A prewet three-ball macro Snyder column was placed atop the concentrator. The concentrator assembly was placed in a hot water bath and concentrated to 6-8 ml within 30 minutes. The apparatus was allowed to cool. The three-ball macro column and evaporatory flask were removed and replaced with a two-ball micro Snyder column and the extraction was further concentrated to approximately 4 ml. The extract was then quantitatively transferred to a vial, diluted to a final volume of 5 ml, and stored at or below 4°C until analyzed.

The second sample was generated using the following procedure. The condensate and condensate rinse samples were combined and transferred to a separatory funnel, spiked, and serially extracted with methylene chloride exactly as was done with the front half rinse.

The porous polymeric resin was transferred to a glass extraction thimble, spiked and processed identical to the particulate matter sample. The condensate and resin extracts were combined, residual water removed, and then concentrated as described above.

Blank samples were extracted concurrently with the collected samples. All samples were spiked with internal standards just prior to analysis.

3.2.7 GC Analysis

Prior to GC/MS analysis, a 1 μl aliquot of the samples was analyzed on a Perkin Elmer 8500 GC system. The system was equipped with a J&W Scientific DB-5 capillary column. This screening procedure checked the concentration of the analytes and determined if dilution or further concentration of the samples was necessary. The GC screening showed that the samples needed to be concentrated to a final volume of 1 ml. Final concentration of the samples from 5 ml to 1 ml was performed as described earlier.

3.2.8 GC/MS System, Calibration and Operation

A GC/MS system was used for extract analysis. The system was temperature programmable and had a splitless injection option. A fused-silica capillary column capable of PAH separation was used. Other CG/MS equipment met specifications, including GC/MS interface, data acquisition system and other ancillary equipment as described in EPA Method 8270.

The GC/MS system was properly hardware-tuned. Background subtraction techniques designed to eliminate column bleed or instrument background ions were available but not utilized as they were not necessary. GC column performance was evaluated and injection port inertness was confirmed. Calibration standards were analyzed and their response factors were calculated and evaluated. A system performance check using approved System Performance Check Compounds was performed and the results evaluated. The percent relative standard deviation of the compounds was calculated as was the linearity of the calibration curve. When the system tuning, the calibration check, the performance check, and the internal standard response data met minimum method requirements, analysis of the samples began. An external calibration curve was generated as a check against the internal calibration.

A Hewlett Packard (HP) Model 5890 Series II Gas Chromatograph was used for analyte separation. The system was equipped with a 30 m x 0.25 mm ID, 1 µm film thickness silicone-coated, fused-silica capillary column; a J&W Scientific DB-5 capillary column. The GC temperature program held the initial temperature at 40° C for 5 minutes to remove the methylene chloride solvent. The temperature was ramped to 280° C at a rate of 6°C per minute and held there for 18 minutes. The Helium carrier gas flow rate was 30 ml/min. This flow rate is lower than that recommended by Method 8270C, causing the analytes of interest to elute at a later time than published in the Method, but this did not present a problem for either identification or quantification. After the system parameters were set, a spiked 1µl aliquot of concentrated extract was injected (splitless) into the GC/MS system. A HP 5971A Mass Selective Detector was interfaced with the GC scanning up to 500 amu per second at 70 volts. The qualitative identifications of compounds determined by this method are based on retention time in the GC and on comparison of the sample's mass spectrum with characteristic ions in a reference mass spectrum. The reference library used was the NBS49K library. Compound identification was not hampered by component coelution; that is, all analytes of interest were sufficiently separated chromatographically. When a compound had been identified, the determination of analyte concentration was based on the integrated abundance from the Extracted Ion Current Profile (EICP) of the primary characteristic ion.

3.2.9 Results

3.2.9.1 Drop-Tube Reactor Results

PAHs in quantifiable amounts were found in all samples collected. Additionally, PAHs were also found in a sample generated by extracting 1g of Middle Kittanning feedstock coal. Table 3.2.3 shows the concentrations in micrograms per megajoule (μg/MJ) of PAHs in the extracts from the recovered solid subsamples at an air to fuel ratio of 1.25/1, and from the feedstock coal. Note that multiplying μg/MJ by 2.33 converts the results to pounds per trillion Btu, another common basis the results are reported in. Table 3.2.4 shows the concentrations in μg/MJ of the PAHs from the recovered liquid and condensed gaseous phase subsamples at an air to fuel ratio of 1.25/1. Table 3.2.5 shows the concentrations in μg/MJ of PAHs in the extracts from the recovered solid subsamples at an air to fuel ratio of 1/1. Table 3.2.6 shows the concentrations in μg/MJ of the PAHs from the recovered liquid and condensed gaseous phase subsamples at an air to fuel ratio of 1/1.

Table 3.2.3 PAH Concentrations (μg/MJ) from Solid Phase Extracts at Air-to-Fuel Ratio of 1.25/1

Analyte	800°C	900°C	1,000°C	1,100°C	1,200°C	1,300°C	1,400°C	Coal
Naphthalene	49	44	50		17		17	39
Acenaphthylene			39					
Phenanthrene	21	23	27	11	18	9	24	17
Fluoranthene			17	5	12			
Pyrene			17	15	23			

Table 3.2.4 PAH Concentrations (μg/MJ) from Condensed Vapor Phase Extracts at Air-to-Fuel Ratio of 1.25/1

Analyte	800°C	900°C	1,000°C	1,100°C	1,200°C	1,300°C	1,400°C
Naphthalene	420	4,871	4,674	7,027	11,371	11,736	4.518
Acenaphthylene			232	737	954	491	73
Fluorene					240	209	92
Phenanthrene				39	264	475	
Anthracene						288	
Fluoranthene				27	35	523	30
Pyrene				26	30	376	
Chrysene						253	103

Table 3.2.5 PAH Concentrations (µg/MJ) from Solid Phase Extracts at Air-to-Fuel Ratio of 1/1

Analyte	800°C	900°C	1000°C	1100°C	1200°C	1300°C	1400°C
Naphthalene	5	69	5	9	12	3	3
Acenaphthylene					1		
Flourene	1	1		1	1		
Phenanthrene	33	13	42	62	51	2	13
Anthracene	1	1		3	3	1	1
Fluoranthene	19	3	4	19	14	2	26
Pyrene	18	3	12	18	15	1	6
Benzo[a]anthracene	16		15	21	13	1	7
Chrysene	39	3	46	76	47	5	16
Benzo[b]fluoranthene	14		17	31	10	1	15
Benzo[k]fluoranthene	14		9	14			9
Benzo[a]pyrene	18		9	46	6		
Indeno[1,2,3-cd]pyrene	19			5			
Dibenzo[a,h]anthracene	1			18	1		
Benzo[g,h,I]perylene	33			39	1		

Table 3.2.6 PAH Concentrations (µg/MJ) from Condensed Vapor Phase Extracts at Air-to-Fuel Ratio of 1/1

Analyte	800°C	900°C	1000°C	1100°C	1200°C	1300°C	1400°C
Naphthalene	1185	875	1090	964	934	652	1023
Acenaphthylene	12			6	12	9	28
Acenaphthene				3	3		1
Flourene	12	3	15	11	19	9	13
Phenanthrene	45	5	64	54	113	59	91
Anthracene	5	1		5	15	6	11
Fluoranthene	61	8	12	6	25	18	56
Pyrene	58	7	16	6	14	17	30
Benzo[a]anthracene	23	2	15	9	30	11	6
Chrysene	32	5	33	22	60	24	10
Benzo[b]fluoranthene	22			6	21	13	
Benzo[k]fluoranthene	23			3	16		
Benzo[a]pyrene		24			12		
Indeno[1,2,3-cd]pyrene	32						
Benzo[g,h,I]perylene	63				15		

Combustion efficiencies were also calculated from analysis of the feedstock coal samples and the collected char samples. Ash content was determined for all samples in a LECO MAC 400 Thermogravimetric Analyzer. Combustion efficiencies were calculated using ash as the tracer. The equation used is:

$$\Delta W = \{1-[A_o(100-A_c)\}/[A_c(100-A_o)]\}*100$$

Where ΔW = Per cent weight loss calculated on a dry ash free basis (% Burnout)
A_o = ASTM ash of the dry feedstock
A_c = ASTM ash of the dry char

The assumption involved in using this equation is that the mineral matter in the coal does not undergo transformations which would change the quantity of ash produced upon ashing the chars. Table 3.2.7 shows the combustion efficiencies for the two air to fuel ratios investigated in the DTR.

Table 3.2.7 DTR Combustion Efficiencies for Varying Air to Fuel Ratios

Temperature	800°C	900°C	1000°C	1100°C	1200°C	1300°C	1400°C
% Burnout, 1.25/1	48.5	65.6	71.4	82.4	77.2	82.1	79.7
% Burnout, 1/1	39.9	55.2	64.3	69.1	70.2	68.4	70.1

3.2.9.2 Demonstration Boiler Results

PAHs in quantifiable amounts were found in all samples collected. Table 3.2.8 shows the concentrations in µg/MJ of PAHs in the extracts from the samples collected upstream of the baghouse. Table 3.2.9 shows the concentrations in µg/MJ of the PAHs from the samples collected downstream of the baghouse.

Table 3.2.8 PAH Concentrations (µg/MJ) from Condensed Vapor Phase Extracts Collected Upstream of the Baghouse

Analyte	HF-HA	HF-LA	LF-HA	LF-LA
Naphthalene	74	31	58	100

Table 3.2.9 PAH Concentrations (µg/MJ) from Condensed Vapor Phase Extracts Collected Downstream of the Baghouse

Analyte	HF-HA	HF-LA	LF-HA	LF-LA
Naphthalene	92	72	76	43
Phenanthrene	2	2	2	1

3.2.10 Discussion

3.2.10.1 Discussion of Drop-Tube Reactor Results

Of the 16 PAH species listed by the EPA as HAPs, only naphthalene and phenanthrene were found to be extractable from the feedstock coal. Since most PAH species are not present as such in the feed, it is not possible to conduct a material balance. It was necessary to investigate the effects of temperature and oxygen concentration on the formation and subsequent destruction of the PAHs. Two series of experiments were conducted across a temperature range of 800°C-1400°C at two different air to fuel ratios. The PAH species were measured from samples in both the solid and condensed vapor phases as described above. PAHs were found in quantifiable amounts in all samples collected.

For the experiments conducted at an air to fuel ratio of 1.25/1, seven of the sixteen HAP PAHs were detected (Miller et al., 2000; Pisupati et al., 2000). It was observed that the vapor phase PAH emission concentrations increased with temperature to about 1,300°C and then dropped dramatically. The emission values reported for the vapor phase PAHs, and in particular those for naphthalene, are extremely high. At 1,300°C, the naphthalene concentration of 11,736μg/MJ represents just under 0.04% (by weight) of the thermal input of the coal. Since the carbon burnout values for these samples are much lower than found in utility boilers, it is not surprising to find the bench scale PAH emissions much higher than those reported from utility boilers (Szpunar, 1992) and other earlier studies including pilot scale combustors (Davies et al., 1992; Pisupati, et al., 1998; Miller et al., 2000).

In contrast to the vapor phase PAHs concentrations, solid phase char sample extracts contained small amounts of PAHs throughout the temperature range. This suggests that when PAHs either form in the solid phase or are liberated from the solid phase, they easily loose their affinity for the solid phase and rapidly enter the vapor phase. It has been reported (Miller et al., 2000; Pisupati, et al., 2000) that up to approximately 1,300°C, the rate of PAH formation and release from the solid phase for this coal exceeds the rate of PAH oxidation in the vapor phase.

There were many monomethyl-, dimethyl- and trimethlynaphthalenes and other similar PAH derivatives identified in the vapor phase of these samples. Their concentrations were not quantified. As the temperature was increased from 800 to 1,200°C, the methyl- aliphatic side chains on the PAHs derivatives were the predominant functional group. At 1,300°C these side chains were converted predominantly to carboxylic acid functional groups, signaling the first stages of PAH oxidation. Above 13,00°C, the rate of PAH oxidation had exceeded the rate of PAH formation, and the PAH concentrations decreased rapidly. Different phenomena were observed at an air to fuel ratio of 1/1.

For the experiments conducted at an air to fuel ratio of 1/1, thirteen of the sixteen HAP PAHs were detected. With the exception of the naphthalene, there are not major differences found in PAH concentrations between the solid phase and vapor phase samples at particular temperatures. There also does not seem to be a trend of individual PAH concentrations varying with temperature. The total amount of quantified PAHs at all investigated temperatures (with the exception of 800°C) is lower in the 1/1 air to fuel ratio sample suite than in the 1.25/1 air to fuel ratio sample suite in both concentration and total mass.

Along with the PAH concentrations, concentrations of the derivative PAH compounds are important to consider. In the suite of experiments where the air to fuel ratio was 1.25/1, the most predominant side chain functional group at lower temperatures was the methyl group. As the temperature increased, the methyl group was oxidized to a carboxylic acid group. In the suite of experiments where the air to fuel ratio was 1/1, the predominant non-oxygen containing side chain functional group at the lower temperatures was 2-propylene. As the temperature increased, the predominant non-oxygen containing side chain functional group became ethylene. These types of side chains can help create larger PAH molecules from smaller ones, and can do so more readily in low oxygen environments. The laminar flow profile of the combustor and the 1/1 air to fuel ratio should create localized areas in the combustor with low concentrations of available free oxygen. Derivative PAH compounds can then more easily become larger PAHs.

In addition to the 16 EPA HAP PAHs, other large PAHs and their derivatives were detected. Anthanthrene, benzo(a)chrysene, and dibenzo(ah)pyrene and their derivatives were detected in appreciable, but unquantified amounts. These large PAHs are hazardous but are not in the EPA HAPs list, probably because they have not been detected in utility boiler flue gas streams.

Oxygen concentration is an important variable in PAH formation. The data suggests that lower oxygen concentrations during combustion leads to higher molecular weight PAH formation along with their precursors and derivatives. The data also suggests that lower oxygen concentrations also retard the release of PAHs and their derivatives from the solid phase to the vapor phase.

Quantified PAH emissions reported from a pilot scale DFC showed only fluoranthene and acenaphthene in detectable limits for the same coal (Miller et al., 2000; Pisupati et al., 2000). These two sets of data show that, at least above 1300°C, the vapor-phase PAH concentrations continue to decrease rapidly with increased particle residence time and increased mixing of air and fuel.

3.2.10.2 Discussion of Demonstration Boiler Results

None of the 16 analytes of interest were found in quantifiable amounts in the solid phase extracts from the samples collected either upstream or downstream of the baghouse. Previously reported data from pilot-scale combustors show slight increases in PAH concentrations with increasing excess-air to fuel ratios, and slight decreases in PAH concentrations with increased firing rate (Miller et al., 2000; Pisupati et al., 2000). Data from the demonstration boiler show slight decreases in PAH concentrations with increasing excess-air to fuel ratios, and slight increases in PAH concentrations with increased firing rate. It is important to note that two of the four data set pairs from the demonstration boiler (i.e., Low Air and High Fuel) are within EPA sampling reproducibility limits. The other two pairs are just above EPA sampling reproducibility limits. The numerical differences from the pairs of demonstration boiler data may be statistically insignificant, and if so the reported trends may also be insignificant. The important differences are found in the types of PAH derivatives present in the demonstration boiler samples and total demonstration boiler PAH concentrations.

As discussed above, lower excess oxygen concentration in the DTR combustor leads to predominantly longer side chains on the PAHs. The only PAH side chains identified for the High Air samples were the methyl and carboxylic acid functional groups. These unquantified PAH derivatives were detected at relatively low concentrations. The predominant PAH side chains identified for the Low Air samples were the methyl, ethyl, carboxylic acid and acetic acid functional groups. These unquantified PAH derivatives were detected at significantly higher concentrations than their High Air counterparts. Therefore similar trends were noted in the types of PAH derivatives between the low (1/1) air to fuel ratio data from the DTR and the Low Air demonstration boiler data, as well as between the high (1.25/1) air to fuel ratio data from the DTR and the High Air demonstration boiler data.

The total amount of PAHs reported from the demonstration boiler is well within the range reported for the down-fired combustor and only slightly higher than the research boiler (Miller et al., 2000; Pisupati el al., 2000). It may well be prudent not to try to over-interpret the demonstration boiler PAH data. There are only minor, possibly statistically insignificant differences between the PAH concentrations reported in many of the samples collected from the demonstration boiler. Other factors that affect the interaction with oxygen to the fuel (particle residence time, gas and temperature profiles), important to PAH formation and release to the vapor phase were not investigated.

3.2.11 Conclusions

A Middle Kittanning seam coal was fired in a bench-scale, laminar flow, drop-tube furnace at a variety of temperatures. Solid, liquid and condensed vapor-phase samples were withdrawn isokinetically from the furnace and analyzed for PAH concentrations using EPA methods. For an air to fuel ratio of 1.25/1, results showed near constant PAH concentrations in the solid-phase samples, while the PAH concentrations in the vapor-phase samples increased as a function of temperature. At a temperature around 1,300°C, it appears that the rate of PAH formation was exceeded by the rate of PAH oxidation, and PAH concentrations in the vapor-phase began to decrease (Miller et al., 2000; Pisupati et al., 2000). For an air to fuel ratio of 1/1, results showed little difference in PAH concentration between the solid phase and vapor phase samples, with the exception of naphthalene. A higher number of PAHs were detected in the lower air to fuel ratio. Increasing temperatures between 800°C and 1400°C did not dramatically affect either PAH formation or destruction. At lowered oxygen concentrations, higher molecular weight PAHs and many more types of PAH derivatives were formed.

A Middle Kittanning seam coal was fired in a demonstration-scale boiler at various air and fuel rates. Solid, liquid and condensed-vapor phase samples were withdrawn isokinetically from the boiler and analyzed for PAH concentrations using EPA methods. Only naphthalene and phenanthrene were detected. The amount of PAHs detected in the demonstration boiler are similar those found in other pilot scale units.

Availability of oxygen is a more dominant factor in PAH formation and destruction than temperature for all units tested. The laminar flow design of the DTR decreases air to fuel mixing as compared to the other combustors investigated. This effectively lowers the amount of