An investigation on polycyclic aromatic hydrocarbon emissions from pulverized coal combustion systems

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Abstract

Results from a series of tests conducted to study the emission of polynuclear or polycyclic aromatic hydrocarbons (PAHs) from bench-scale and small industrial, water-tube boiler are discussed. A Middle Kittanning, and Upper Freeport seam coals were used in the study. Samples were extracted from the reactor outlet and from the inlet and outlet sides of the research boiler's (RB) baghouse using EPA promulgated methods.

Only acenaphthene and fluoranthene were detected in down-fired combustor (DFC) samples. In addition to these two, naphthalene was detected in the RB samples. Emission factors ranged from 80 to 320 μg/kg of fuel fired. Although there were minor trends in the emissions' data, given the reproducibility limits for PAH compounds, no significant differences were found in the emissions with respect to the fuel type or form (pulverized coal (PC) vs. coal–water slurry fuel (CWSF), and raw vs. cleaned coal) and firing conditions (high and low excess air). The PAH emissions showed a decrease with increase in the firing rate.

A bench-scale drop-tube reactor (DTR) was used to study the effects of temperature and residence time on PAH formation. The results revealed 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 of around 1300°C, the rate of PAH formation was exceeded by the rate of PAH oxidation, and PAH concentrations in the vapor phase began to decrease. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Title III of the Clean Air Act Amendments (CAAA) of 1990 contains provisions that require the US EPA to promulgate emission standards for the 188 compounds or groups 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. This would result in regulated sources sharply reducing routine emissions of toxic air pollutants. Nine major categories of polycyclic organic matter (POM), alternatively referred to as polynuclear or polycyclic aromatic compounds (PACs) have been defined by EPA [1]. The study of organic compounds from coal combustion is complex and the few results published so far are inconclusive with respect to emission factors (Curtis et al., 1993; [2]). Since most POM is formed and destroyed during combustion, our inability to conduct a material balance makes it difficult to come up with reliable emission factors. Data under varying combustion conditions are necessary to establish reasonable regulatory guidelines. The most common organic compounds in the flue gas of coal-fired power plants are polynuclear or 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-c,d]pyrene, benzo[g,h,i]perylene, and dibenz[a,h]anthracene. Penn State is currently conducting a comprehensive study of the emissions from coal combustion, and is well equipped to collect and analyze most of the HAPs in combustion flue gases.

2. Objectives

The overall objectives of this study were to measure the emissions from and determine the effect of temperature on the formation and destruction of PAH in pilot-scale coal combustion systems. Monitoring was limited to the 16 EPA-specified priority hazardous pollutants.

3. Experimental

The study used two pilot-scale combustion systems and a bench-scale drop-tube reactor (DTR). The pilot-scale combustion systems were: a pilot-scale 146 kW down-fired combustor (DFC), and a 454 kg/h (steam) industrial research boiler (RB).

The DFC (Fig. 1) was designed to evaluate the combustion performance of, and pollutant emissions from, various fuels (natural gas, coal, coal–water slurry fuels (CWSF)). The combustor has a 0.5 m internal diameter, and is 3 m high. Each module consists of five 0.53 m tall and 0.5 m diameter circular refractory sections. A divergent refractory cone, commonly called a quarl, is positioned on top of the four circular refractory sections. The divergent cone top has a half-angle of approximately 10° and is fitted with a multi-fuel burner. The combustor is lined with a 0.076-m thick refractory
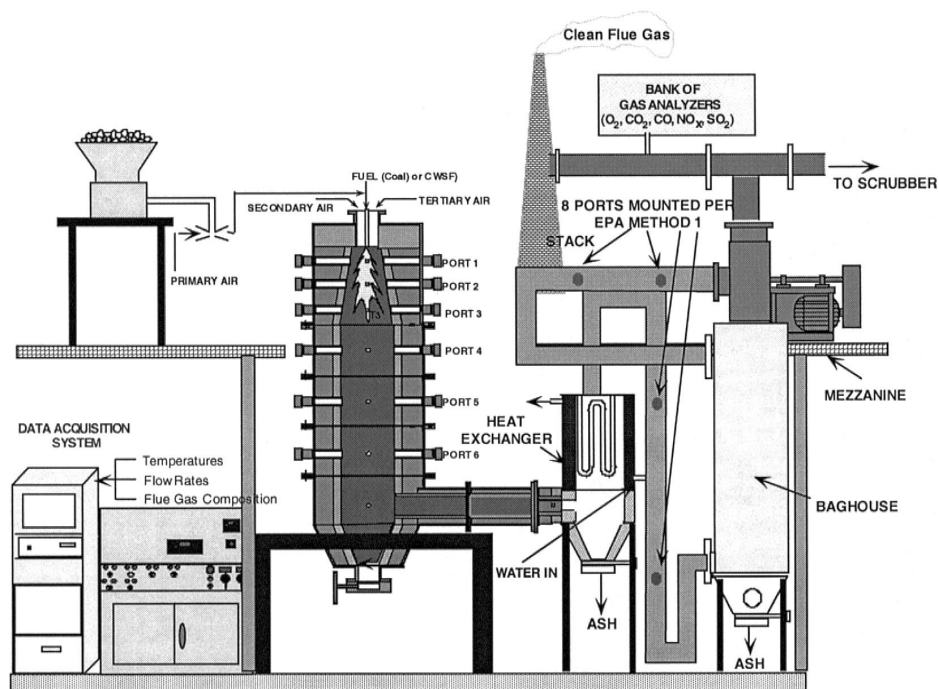
Fig. 1. Schematic diagram of the DFC.

material to withstand temperatures up to 1650°C. An 8-in. thick, light weight, high alumina insulation layer was used to minimize heat loss and produce a flame temperature between 1450°C and 1500°C. The flue gases pass through a modular heat exchanger that cools them to about 100°C before they exit. Several 0.01 m diameter sampling ports are located along the axis of the combustor. Sample ports are numbered 1 through 10 starting at the top. Gas samples for compositional analysis were extracted at the exit of the heat exchanger. Wall temperatures were monitored with type-S thermocouples at six locations along the combustor. The temperature of the flue gas entering and leaving the heat exchanger is monitored with type-K thermocouples. Coal was transported by primary air constituting 10% of the total combustion air. Secondary air was introduced into the annular secondary pipe, which usually constituted 30% of the total air. The balance of the combustion air was introduced as tertiary air. All air streams entered at the same height.

A schematic diagram of the 454 kg/h (steam) RB is shown in Fig. 2. The boiler is a 10 bar working pressure, A-Frame water-tube boiler, designed and built by Cleaver Brooks. The combustor is a $0.91 \times 0.91 \times 2.1$ m chamber with a maximum heat release rate of 350 W/m^3. It contains 26.75 m^2 of heating surface and the maximum fuel firing rate is 0.586 kW. The boiler is equipped with 18 side ports for gaseous and particulate sampling. Fourteen of the ports have diameters of 0.071 m and four have diameters of 0.1 m. The combustion gases split into two convective passes, one on each side of the radiant combustion chamber. There are access doors into each of the convective
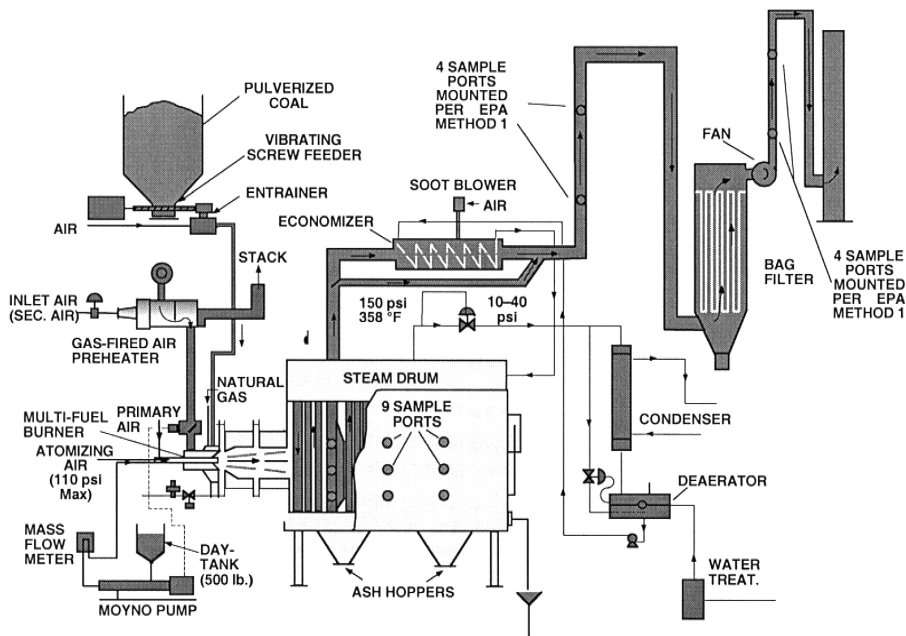
Fig. 2. Schematic diagram of the RB.

sections. There are also two ash hoppers under each convective section and there is an access door into the radiant combustion chamber.

To promote and enhance combustion, a ceramic burner throat extends the combustion chamber length by 0.6 m. This ceramic section, termed a quarl, is preheated by a natural gas flame prior to pulverized coal (PC) combustion. This supports hard-to-ignite fuels by storing some of the radiant energy released by the flame. The PC is fed by a screw feeder from a 40 kg capacity hopper, to an eductor and then transported by compressed air into the burner.

The DTR is a vertical, electrically-heated reactor that simulates the heating rate, temperature profile, and particle residence time of a utility boiler. The DTR contains an alumina muffle tube, 6.35 cm in internal diameter and 95.25 cm long, with a maximum temperature $(1550°C)$ zone of 50.8 cm. However, selected operating temperatures for this study were between $800°C$ and $1400°C$. 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 approximately 25–30% excess air for the selected coal feed rate.

3.1. Test matrix

The first series of tests was conducted in the 146 kW DFC to determine the effect of firing rate and level of excess air on PAH formation. A Middle Kittanning seam coal

Table 1
Summary of the tests conducted

Combustor	Fuel	Fuel form	Firing rate (kW)
DFC	Middle Kittanning	PC	125
DFC	Middle Kittanning	PC	92.3
DFC	Middle Kittanning	PC	92.3
DFC	Freeport (raw)	PC	92.3
DFC	Freeport clean	PC	92.3
DFC	Freeport clean	PC	92.3
DFC	Middle Kittanning	CWSF	92.3
DFC	Middle Kittanning	CWSF	92.3
RB	Middle Kittanning	PC	468
RB	Middle Kittanning	PC	468
RB	Middle Kittanning	CWSF	468
RB	Middle Kittanning	CWSF	468

was pulverized to 80% passing 200 mesh (pulverized coal or ''PC'' grind). The coal was fed into the combustor at two rates: 92.3 kW (designated ''low fire'') and 124.5 kW (designated ''high fire''). The combustion air was monitored by the oxygen concentration in the flue gas stream. The excess oxygen was held at either 3% (designated ''low air'') or 5.5% (designated ''high air'').

The second series of tests investigated the effect of fuel type and form on PAH emissions. All fuels in this series of tests were burned under low fire, high air conditions. Freeport seam raw and cleaned coals were prepared as PC and burned in the DFC. Additionally, the Middle Kittanning coal was re-tested at these conditions, but with a slightly different temperature profile in the combustor than in the earlier test. Finally, the Middle Kittanning coal was tested as a CWSF in the DFC.

A third series of tests was conducted to establish the effect of combustor scale on PAH formation. The Middle Kittanning coal was tested as both PC and CWSF in the RB. Table 1 summarizes the test matrix. The coal studied in detail under controlled conditions in a vertical, electrically heated DTR was the Middle Kittanning seam coal.

4. Analytical methodology

A modular 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 the various parameters needed for isokinetic sampling of the combustors. 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 performed by EPA Method 3540-C. Extraction of PAHs from the collected liquid fraction was done by EPA Method 3510-C. Sample cleanup was accomplished by EPA Method 3630-C.

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 combustor through a heated probe, where the particulate matter was filtered out of the stream. The

remainder of the sampled gas 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, listed in order from upstream to downstream. A straight stainless steel nozzle is located at the end of the sampling probe. The nozzle opening and yaw angles of 0° is placed into the flue gas facing upstream. 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, which contains heating elements. While sampling, the probe was maintained at 121°C by a temperature controller. The seal between the combustor/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 121°C. A filtering medium 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 the 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 20°C. 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. All samples were collected within the acceptable sampling range of 90% to 110% of isokineticity.

5. 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 and 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 chemically similar to the analytes of interest, but not expected to be present 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 30 min for approximately 18 h.

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 greater than 11 with sodium hydroxide and serially extracted three more times. The pH was then adjusted to less than two 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 pre-wet 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 min. 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. It 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 as was done with the front half rinse.

The porous polymeric resin was transferred to a glass extraction thimble, spiked, and processed in an identical way 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.

6. Gas chromatography / mass spectrometry (GC / MS) system evaluation

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 GC/MS equipment met EPA Method 8270 specifications, including GC/MS interface, data acquisition system, and other ancillary equipment.

The GC/MS system was properly hardware-tuned. Background subtraction techniques designed to eliminate column bleed or instrument background ions were available but were not needed. 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.

7. GC analysis

Prior to GC/MS analysis of the samples, a 1 μl aliquot 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 to 1 ml was performed as described earlier.

8. GC/MS analysis

A Hewlett Packard (HP) Model 5890 Series II gas chromatograph was used for analyte separation. The system was equipped with a 30 m × 0.25 mm ID, 1 μm film thickness silicone-coated, fused-silica capillary column (J&W Scientific DB-5). The GC temperature program held the initial temperature at 40°C for 5 min 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 min. 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 1 μl aliquot of concentrated extract was injected (splitless) into the GC/MS system. An HP 5971A mass selective detector was interfaced with the GC scanning up to 500 amu per second at 70 V. 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 NIST49K reference library was used. Compound identification was not hampered by 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.

9. Results and discussion

From both the DFC and RB, PAHs in quantifiable amounts were only found in the samples prior to the baghouses, and then only in the subsamples collected upstream of the filtering media. Not surprisingly, PAH concentrations in the subsamples collected downstream of the filter paper in the sampling train yielded concentrations below the detection limits. The most probable explanation is that the PAHs have boiling points well above 121°C, the temperature maintained at the particulate filter assembly. The PAHs would tend to condense on the probe itself, on the char particles, or on the filter paper. Thus, no PAH species were detected in quantifiable amounts in subsamples downstream of the particulate filter assembly.

The effect of fuel type was investigated by firing raw and cleaned Freeport coals and the Middle Kittanning coal. It is important to note that the ash contents of the Upper Freeport raw and cleaned coals are 25.99% and 7.69%, respectively (Table 2). Fig. 3 shows the emissions of acenaphthene and fluoranthene. No other PAH species was detected in the samples. The emissions of both were between 31.8 to 51.7 $\mu g/MJ$, which were within the reproducibility limits of the methods.

In the DFC, no PAHs were detected in quantifiable amounts in any sample collected downstream of the baghouse. The low gas velocities in the DFC after the baghouse did not permit proper particulate matter sampling. These low velocities (averaging approximately 1.5 m/s) permit entrainment of even the smallest of particles. Many of the particulates may even collect in areas of the ducting where the velocities are even lower than 1.5 m/s. The temperature in the ducting just downstream of the sampling port averaged about 121°C. Any PAHs entrained in the flue gas stream coming into contact with the duct walls would probably condense on the walls. The high efficiency of the baghouse, low flue gas velocities, and low flue gas temperature contribute to lowering the (potential) PAH concentration in the flue gas stream. Thus, no measurable amount of particulate material was obtained from DFC stack sampling, and no PAHs above the detection limit were observed in these samples. There were no quantifiable amounts of

Table 2
Compositional analysis of the fuels

Proximate analysis (wt.%)

Sample	Moisture (raw)	Ash (dry)	Volatile matter (dry)	Fixed carbon (dry)	HHV (MJ/kg) (dry)
Freeport (raw)	1.81	25.99	26.47	47.54	24.41
Freeport (cleaned)	1.73	7.69	32.21	60.10	31.71
Middle Kittaning	1.99	5.11	30.53	64.36	32.88

Ultimate analysis (wt.%)

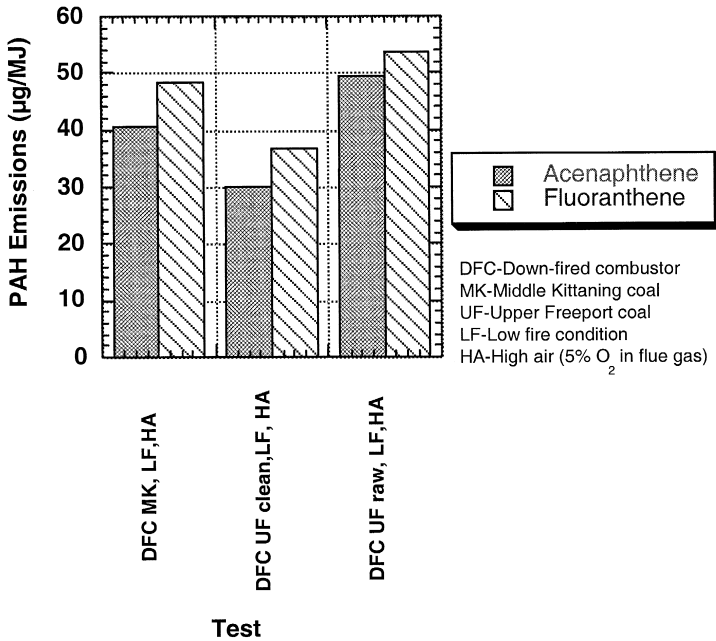|	Carbon (dry)	Hydrogen (dry)	Nitrogen (dry)	Sulfur (dry)	Oxygen (dry)
Freeport (raw)	60.67	4.13	1.10	1.87	6.23
Freeport (cleaned)	77.99	5.10	1.38	1.47	6.37
Middle Kittaning	80.41	4.84	1.41	0.72	7.51

Fig. 3. Effect of fuel type on the PAH emissions.

PAHs detected in any of the samples collected downstream of the baghouse in the RB. The gas velocities in the RB are approximately 18.3 m/s and the temperature is somewhat higher, 176°C. Still, barely measurable amounts of particulate matter were collected at this location. The particulate matter collected prior to the baghouse from both the DFC and the RB contained PAHs in quantifiable amounts. Fluoranthene, acenaphthene, and naphthalene were found in all RB samples collected prior to the baghouse. Fluoranthene and acenaphthene were found in all DFC samples collected prior to the baghouse. Therefore, no significant effect of fuel type was observed with the fuels examined.

Most of the PAH species form by a pyrosynthesis mechanism at relatively lower temperatures. Data in Fig. 4 indicate that the CWSF fuels emitted slightly higher PAHs than the PC. This is possibly due to the temperature differences in the combustion chamber. The heat required to vaporize the water in micronized coal water mixture (MCWM) is 3–4% of the heat of combustion and as such had no substantial impact on the overall combustion process. However, according to the sequential steps involved in the combustion of coal water slurry droplets, there is a drying period during which the droplets are heated and their moisture content is evaporated [5]. Difficulties in ignition are often due to the fact that water evaporation is occurring at the outset of the process of MCWM combustion [4]. Walsh et al. [7] determined that the time to ignition (approximately 5 ms for an 80 μm droplet) is approximately double that required for a dry coal particle. The distance from the burner at which ignition occurs for the MCWM has been estimated to be double that for PC [7].
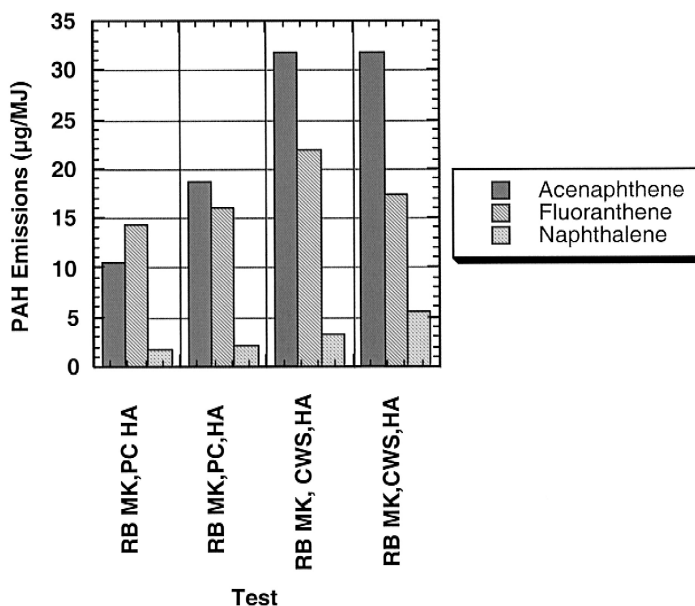
Fig. 4. Effect of combustion conditions on PAH emissions.

The two combustors have different gas residence times and temperature profiles. Table 3 shows the gas residence time distribution in the DFC. The total gas residence time is computed to be about 3.1 s at a firing rate of 102 kW. The gas residence time in the RB is about 3 s. The gas temperatures in the RB were measured using suction pyrometry when firing micronized coal (MC) and MCWM, and are given in Fig. 5. The three dimensional schematic diagram of the boiler is used to provide an accurate perspective of the location of the measurements and also to illustrate the location of the observation ports. The temperature difference remained about the same from the front (exit of the quarl) to the back of the boiler in the radiant section (156°C). The gas

Table 3
Mean gas residence times in the DFC

| Zone	Distance from the burner (m)	Residence time at various firing rates (s)				
		176 kW	146 kW	132 kW	117 kW	103 kW
Burner quarl–Port 1	0.47	0.026	0.0316	0.0335	0.0395	0.045
Port 1–Port 2	0.78	0.088	0.105	0.117	0.131	0.15
Port 2–Port 3	1.08	0.115	0.138	0.153	0.173	0.198
Port 3–Port 4	2.17	0.459	0.551	0.613	0.689	0.787
Port 4–Port 5	2.65	0.362	0.432	0.483	0.543	0.62
Port 5–Port 6	3.16	0.369	0.434	0.492	0.553	0.632
Port 6–Outlet	5.70	0.383	0.466	0.511	0.574	0.656
Total	5.70	1.80	2.16	2.40	2.70	3.10
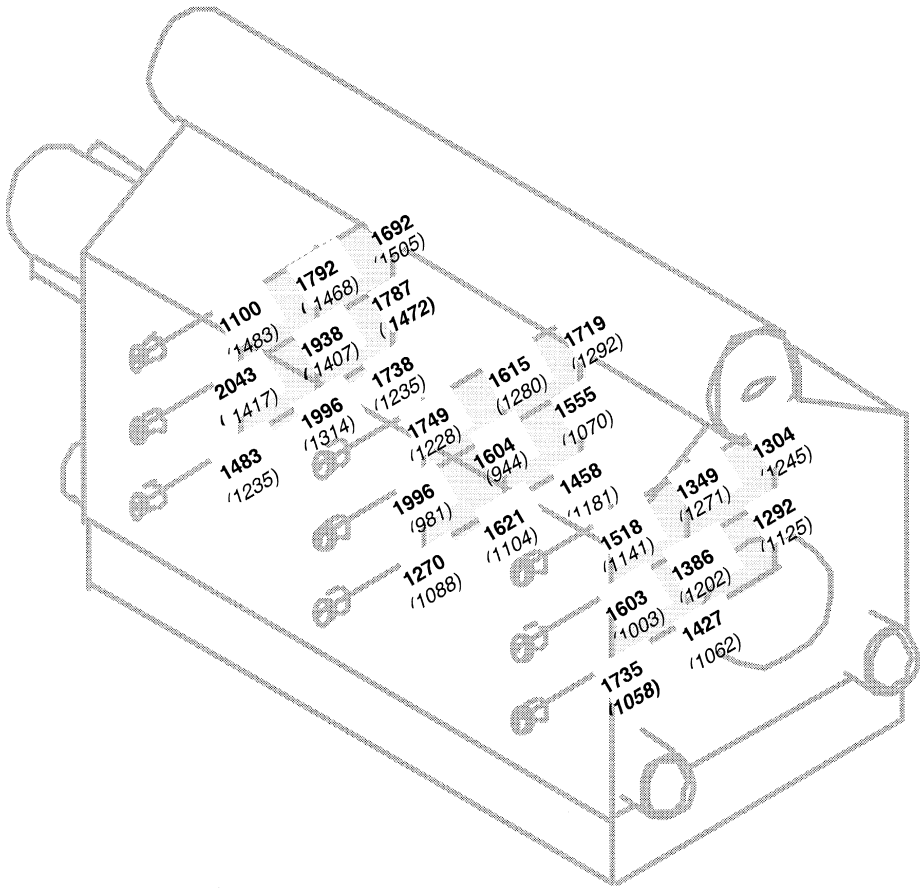
Fig. 5. Temperature measurements in the RB when firing micronized coal and coal water mixture.

temperature in the case of MC firing was higher than that in the MCWM test. This was partly due to evaporation of water in the latter case. The average difference in the temperature measured across a vertical plane in front of the boiler for the MC and MCWM was about 169°C, and remained about the same from the front (exit of the quarl) to the back of the boiler in the radiant section (156°C). Higher mean gas temperatures in the front of the boiler indicate more rapid ignition and a higher rate of combustion, hence, a higher heat release rate.

Gas temperature profiles (as measured by suction pyrometry) in the DFC when firing PC varied as a function of time. The gas temperature varied from 1310–1425°C at Port 2 to 870–900°C at Port 6. These peak temperatures are slightly higher than those in the RB. The residence time is higher in the DFC. However, the results are still within the reproducibility of the PAH analysis.

Fig. 6 shows the effect of the combustion conditions in the DFC on the emissions of acenaphthene and fluoranthene. As the excess air and firing rates were increased in the
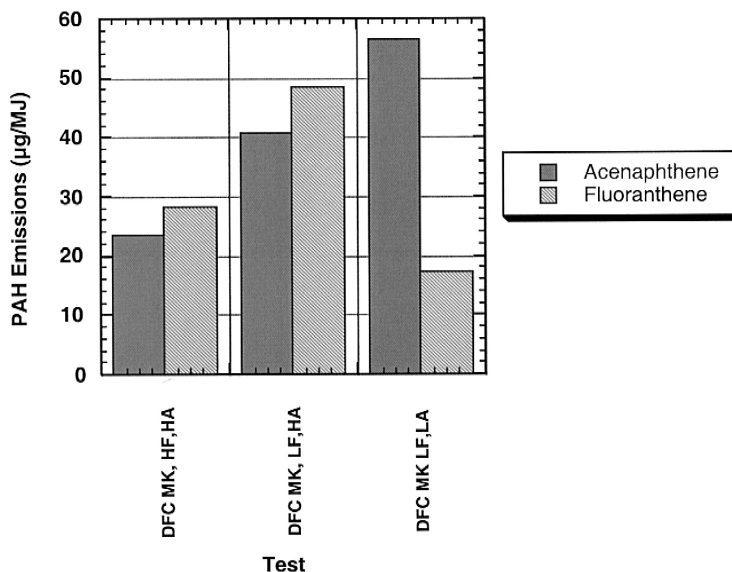
Fig. 6. Effect of combustion conditions on PAH emissions in the DFC.

DFC, the PAH concentrations were again within the reproducibility limits. It is important to note that in most of the large-scale units, there is a significant amount of air leakage into the combustion chambers. For the DFC, based on the actual air flow rates and the outlet oxygen measurements, it was observed that there was air leakage of about 20% of the stoichiometric air requirement (at a firing rate of 146 kW). The exact location of air leakage is not certain. For low and high fire conditions in this study, the oxygen levels in the flue gas were 3% and 5%, respectively. This includes the air leakage. The data indicate that the increase in the excess air above the 3% oxygen level in the flue gas did not produce any changes in the emission behavior of PAHs.

Fig. 7 shows the emission of acenaphthene, fluoranthene, and naphthalene for the two firing rates in the DFC and at 469 kW in the RB. A general trend of increasing PAH emissions with decreasing firing rate was observed. For both PC and CWSF, increasing the size of the unit decreased the concentration of PAHs present. PAH concentrations were much higher for CWSF than for PC. Szpunar [6] reported a similar trend in PAH emissions from three power plants ranging in size from 350 to 720 MW(e). The emission factors ranged from 85 to 320 μg/kg, while Davies et al. [3] reported an estimated emission factor of 20 μg/kg (total PAH species). These values are much lower than those observed in the current study and are also lower than those reported by Szpunar [6]. Based on the reported values from large power plants and those obtained in this study, it can be observed that higher firing rates and the larger unit sizes produce lower concentrations of PAHs. Fluoranthene was reported to be present in the highest concentration in this study and in emissions from coal-fired power plants. Table 4 gives a comparison of the emission factors determined in this study and those reported by EPA. The values in this study are higher by three orders of magnitude because of the
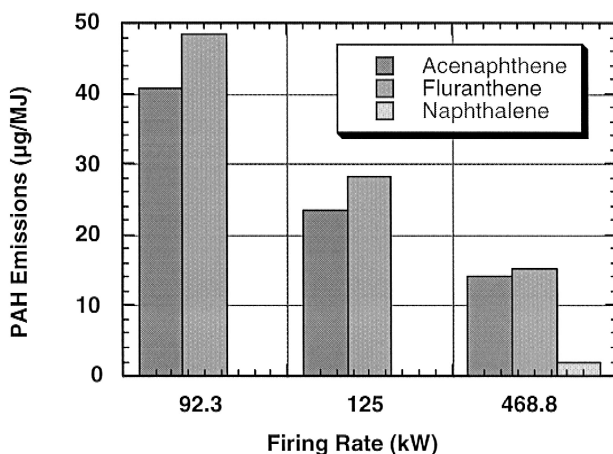
Fig. 7. Effect of firing rate on PAH emissions during pulverized coal combustion.

sampling location. At the outlet of the baghouse, PAH species were below detection limits.

9.1. Effect of temperature in the DTR

The operating temperature and residence time at the operating temperature varies for different boilers and combustors. Since PAH species are not present as such in the feed, it is not possible to conduct a material balance. It is therefore necessary to study the temperature at which PAH species are formed and oxidized in the products (gaseous and solid char). Therefore, a controlled set of experiments was conducted in the DTR (described above). The main objective was to elucidate the influence of temperature on the generation and destruction of PAH species. The DTR was operated at the same air and fuel flow rates but at different temperatures ranging from 800–1400°C. The PAH species were measured in both the solid and gaseous phases as described above. PAHs in quantifiable amounts were found in all samples collected. Additionally, PAHs were also found in a sample generated by extracting 1 g of Middle Kittanning feedstock coal.

Table 4
Comparison of PAH emission factors $(\mu g/Mg)^a$

Study	Acenaphthene	Fluoranthene	Naphthalene
This study[b]	8.200E − 04	1.0900E − 03	7.5200E − 05
EPA emission factor[c]	2.65000E − 07	3.5500E − 07	6.5000E − 06

[a] Note: measurements in this study are at the inlet to the baghouse, whereas the EPA factors are at the outlet of the emission control device.

[b] Average emission factor for three coals tested in the DFC and the RB.

[c] Factors developed from emissions' data from six sites firing bituminous coal, four sites firing sub-bituminous coal, and from one site firing lignite.

It was found that acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene and naphthalene were present in the vapor phase for the temperature range investigated. Fig. 8 shows the PAH emissions in the vapor phase as a function of time. It was observed that the PAH emissions increased with temperature to about 1300°C and then dropped dramatically. It is noted that the reported emission values (μg/MJ), particularly for naphthalene, are extremely high. Many monomethyl-, dimethyl-, and trimethylnaphthalene derivatives were also identified in the vapor phase but were not quantified. Note also, however, that the highest vapor-phase naphthalene concentration at 1300°C of 11,736 μg/MJ represents less than 0.04% (by weight) per MJ of heat input of the Middle Kittanning coal, and that the burnouts for these samples are much lower than one would find in a utility boiler. It is therefore not surprising that the bench-scale PAH emissions are higher than those reported from some utility boilers [6].

Fig. 9 is a plot of PAH concentrations in the char samples as a function of temperature. In contrast to the vapor-phase PAH concentrations, solid-phase char sample extracts contained small amounts of PAHs at all temperatures investigated. This would suggest that when PAHs either form in the solid phase or become liberated from the solid phase, they easily lose their affinity for the solid phase surface and rapidly enter the gas phase. In general, their concentrations increase rapidly until about 1300°C, after which their concentrations drop considerably. It is suggested that up to approximately 1300°C, the rate of PAH formation and release from the solid-phase particles for this
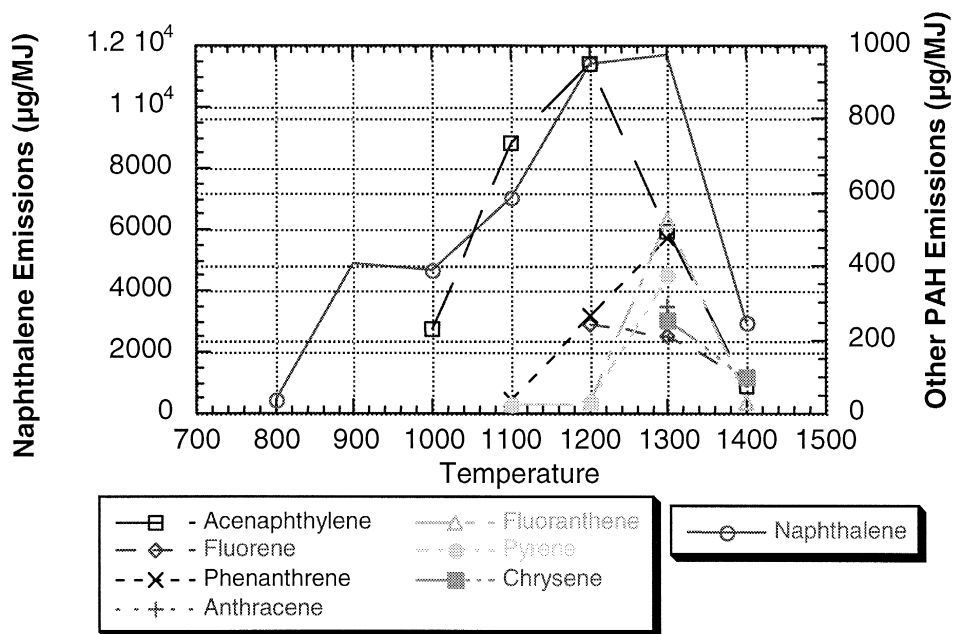

Fig. 8. PAH emissions in the vapor phase as a function of temperature in the DTR.
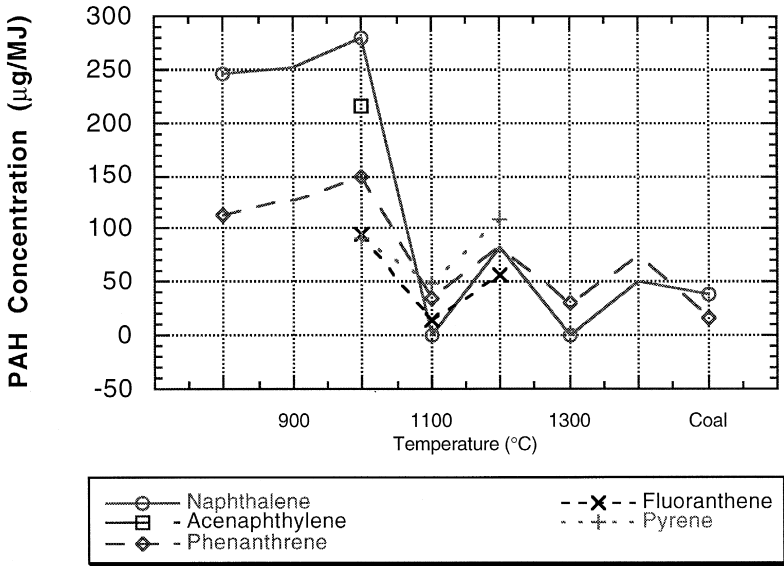
Fig. 9. PAH emissions in the solid phase as a function of temperature in the DTR.

coal exceeds the rate of PAH oxidation in the vapor phase. It is also interesting to note that compounds containing carboxylic acid functional groups appeared in detectable and appreciable quantities in both solid-phase and vapor-phase samples beginning with the 1200°C samples. This oxidation (of the char particles) would account for the fairly constant values of burnout reported between 1100°C and 1400°C, while the PAH concentration in the vapor phase was changing drastically.

Quantified PAH emissions from the DFC showed only fluoranthene and acenaphthene in detectable limits for the same coal. These PAHs were only detected in the solid-phase samples. Using these two sets of data, it is predicted that the vapor-phase PAH concentrations should continue to decrease rapidly with increasing particle residence time.

10. Conclusions

A Middle Kittanning seam and an Upper Freeport seam coal were fired in a pilot-scale down fired combustor and a small industrial boiler. Flue gas samples prior to and after the baghouse were drawn isokinetically and the samples were analyzed for PAH concentrations, generally following EPA methods. Only acenaphthene and fluoranthene were detected in the DFC samples. In addition to the aforementioned, naphthalene was detected in the RB samples. Emission factors ranged from 80 to 320 μg/kg of fuel fired. Although there were minor trends in the emissions data, given the reproducibility limits for PAH compounds, no significant differences were found in the emissions with respect to the fuel type or form (PC vs. CWSF, and raw vs. cleaned coal), firing

conditions (high and low excess air). The PAH emissions showed a decrease with increase in the firing rate.

The influence of combustor temperature was investigated in a DTR. The results revealed 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, of around 1300°C, the rate of PAH formation was exceeded by the rate of PAH oxidation, and PAH concentrations in the vapor phase began to decrease.

Acknowledgements

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