Investigation of Polycyclic Aromatic Hydrocarbons in Fly Ash from Fluidized Bed Combustion Systems

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A laboratory scale fluidized bed reactor and a bench scale 0.1 MW_{th} fluidized bed combustor were used to study the effect of operating conditions on the formation of Polycyclic Aromatic Hydrocarbons (PAHs) in fly ash from fluidized bed combustion systems. A high volatile bituminous coal was chosen to investigate PAH emissions during the entire pyrolysis to oxygen-rich combustion process. During the experiments, the fluidized bed reactor was operated at temperatures between 700 °C and 900 °C, while the excess air ratio was varied from 0 to 1.3. An extraction and GC/MS analysis of PAHs was used in this study. Approximately 40 different PAHs were identified during the tests, of which only a few are specified by the U.S. EPA. The experimental results indicate the majority of the PAHs in the solid phase (bed and fly ash) are derived from the breakdown reactions during the processes of combustion and/or pyrolysis in a Fluidized Bed Combustion (FBC) system, although FBC systems have an efficient solidgas mixing process and relatively long residence time. The total amount of PAHs in the fly ash was much higher than that in the raw coal and in the gas phase. Threeand four-ring aromatic compounds were the major PAHs from pyrolysis conditions, while naphthalene (two-rings) is the dominant compound in bed ash collected from oxygenrich combustion conditions. Only naphthalene was detected in the bed ash in the FBC system. High-speed secondary air (air staging) injected into the freeboard of the FBC system is an effective method for minimizing PAH emissions, along with the other benefits including minimizing NO_x and SO_x emissions.

Introduction

Coals are derived from plant material such as cellulose, lignin, resins, spores, leaves, stems, and roots under intense heat and pressure. The organic matter of coal is generally regarded as being composed of two complementary structures (1-4). The dominant component is a macromolecular, insoluble, three-dimensional network composed of condensed aromatic and hydroaromatic units connected by ether or thioether linkages and short alkyl bridges. The second structure is a molecular phase of compounds which are typically soluble in organic solvents. This molecular phase contains varying distributions of aliphatic hydrocarbons, polycyclic aromatic and hydroaromatic hydrocarbons, hydroxylated polycyclic aromatic compounds, and heterocyclic compounds.

In the atmosphere, PAHs are mainly associated with aerosols (dispersions or suspensions of solid particulate), liquid drops, or a mixture of both (5). The main source of concern with this class of compounds is that some members are known mutagens or carcinogens. PAHs have a strong electrophilic character and interact with biological nucleophyles in metabolic processes. The result of such interactions may obstruct their regular functions and promote carcinogenesis due to transformation of PAHs into diolepoxides of aromatic rings inside the organism (6). To date, the U.S. EPA has prioritized 16 PAH compounds as hazardous air pollutants; these compounds are acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo-[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene (7).

Most PAH formation and emission is associated with soot emissions during the incomplete combustion of fossil fuels (such as start-up and shut down process of combustion facilities including troubleshooting) and as a consequence of the pyrolytic process that precedes combustion (8, 9). Also, as a consequence of the thermion process and by cyclization and aromatization reactions, other aromatic clusters can be developed (10, 11). It has been experimentally shown that it is possible to synthesize benzo[a]pyrene from ethane under pyrolysis conditions (3). When coal is heated, its structure undergoes chemical and physical changes, and organic fractions are released. These fractions undergo cyclization reactions leading to polycyclic compounds that can exist in gaseous and in solid phases, depending on the surrounding temperature and their molecular volume (12-14). They can exist in the gas phase (<4-ring PAHs), in the solid phase (>6-ring PAHs), or in both phases (four- and five-ring PAHs) in the air depending on their molecular mass (15).

Fluidized bed combustion technology has been widely used throughout the world in an effort to reduce sulfur oxide emissions at low cost compared to conventional pulverized combustion (PC) and vortex combustion boilers. The major advantages of fluidized bed combustion (FBC) of fossil fuels are (1) low SO₂ emission due to absorption by limestone directly in the combustor; (2) low NO_x emission due to low combustion temperatures; (3) fuel flexilibility, while even burning low rank coal; and (4) combustion stability with low CO emission levels through high turbulence between solids and gases in the combustor.

The distribution and relative abundance of PAHs arising from fluidized bed combustion (FBC) is a function of operating temperature and process conditions (16-18). The emission of small unburned fragment of coal or char due to incompleted combustion can be minimized by optimizing combustion parameters. Published information (19-21) about operating FBC systems to reduce PAH emissions is still limited. Also, most attention has been paid to PAH emissions in the gas phase emitted in the flue gas. However, PAHs adsorbed on solids (fly ash and bed ash) also can cause pollution when they evaporate into atmosphere. To better understand how to control and reduce the emission of PAHs during coal combustion and pyrolysis, the identification of PAHs, their concentrations, and modes of emission must be known. For environmental reasons it is necessary to know the amount and distribution of PAHs so that appropriate treatment procedures may be followed. The study reported in this paper focuses on the effect of operating conditions on PAH production in fly ash.

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Lab-scale

FIGURE 1. The schematic diagram of WKU-FBC facility used in this study.

Experimental Section

This study was conducted with a laboratory scale stainless steel fluidized bed reactor (i.d. of 45 mm and height of 95 mm) and a 0.1 MW_{th} (heating capacity, 0.3 m i.d.) bench scale FBC combustor, as shown in Figure 1.

Lab-Scale FBC Reactor. The lab scale bubbling FBC reactor was mainly used for pyrolysis without oxygen (N2 as carrier gas) or excess air ratio less than 1 (air and N2 as carrier gas) to simulate the start up and shut down processes of boilers. The lab scale reactor was installed in an electric furnace, preheated to the desired temperature. The premixed (nitrogen and/or air) gas, total 3 L/min, was injected into the reactor through the distributor which was in the bottom of the reactor. Coal with a particle size <40 mesh (150 g) was fed into the combustor at a steady rate from the top of the reactor through a mechanical auger at a rate of approximately 0.5 g/min. The carbon utilization efficiency is typically less than 70%. During the test, no limestone was fed into reactor with coal. All the effluent gas was drawn to a vent with a vacuum pump after it went through a sampling line. The sampling line, which was a modified EPA Method 5-type, includes a high temperature (400 °C) cyclone to collect the particulate matter. The reaction products were swept into the sampling line containing a 37 mm nylon and Teflon filter, a 20 cm condenser, and a tube filled with 1.0 g of Tenax. The tars emitted from the furnace during pyrolysis were collected by the filter and condenser. Precleaned Teflon tubing, glassware, and holders of sampling materials were used in the trapping line. Before each sampling, the Tenax and filters was kept at 150 °C for 1 h to remove any contamination of organics. The effect of temperature and excess air ratio on the formation of PAHs was studied during the pyrolysis study.

The 0.1 MW_{th} Bench Scale FBC Facility. Major combustion studies (excess air ratio > 1.0) were conducted with the bench scale bubbling FBC system similar to the normal operation of a boiler. The Western Kentucky University 0.1 MW_{th} bench FBC system has a 0.3-m i.d. and 4.0-m effective height, using limestone as the bed material in the system. In this study, an under-bed continuous fuel/limestone (particle size <4 mesh) feeding system was installed 0.1 m point above the air distributor in the FBC system. Six moveable heat exchangers in the bed area were also added. Typical operation of the FBC system involves setting the correct coal/limestone feeds and air flows and then using the moveable tubes to adjust the bed temperature to the desired setting. Another 66 gas heat exchange tubes are in a fixed position located approximately a half meter from the top of the combustor to protect the wet cyclone. The operating parameters (air/ water flow, coal/lime feed, bunker weight, temperatures, and pressure) are controlled and logged to file with a computer controller. A Shimadzu GC-8A gas chromatograph was used to continuously monitor the concentration of oxygen, carbon monoxide, and carbon dioxide in the flue gas during the tests. The results were used to adjust the coal and limestone feeding rates and combustion air flow rate.

Fly ash was collected using a high efficiency cyclone at a high temperature (~400 °C) at the outlet pipe 8 h after changing test conditions and the combustor had stabilited. The bed ash was removed from the distributor. The solid samples collected were extracted using a Tecator Soxtec 1045 extraction system. In each run, 15 g of the -60 mesh (250 μ m) ash was placed in the extraction thimble with dichloromethane. The extractor was heated to 120 °C to extract materials from the ash over a period of 1 h. Then, the thimble and ash were removed from the apparatus, and the extract was heated with the refluxing dichloromethane (80 mL) for another 5 h. The extracted solution was condensed and transferred to a 10 mL volumetric flask. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62 000 compound database was used for GC/MS analysis. Aliquots of 2 μ L of sample were injected in the splitless mode onto RTX-5 fused silica capillary column (60 m \times 0.32 mm and a stationary phase thickness of $1.0 \,\mu$ m). Helium was used as the carrier gas. The surrounding temperature for injector, interface, and detector was 230 °C. The mass spectrometer was operated in the selected ion monitoring (SIM) mode for each PAH (EPA Method 8270). The detection limit is 0.1 ppb when the selected ion monitoring (SIM) mode is chosen. The temperature of the gas chromatography oven was programmed from 70 °C to 150 °C at a rate of 8.0 °C/min and then to 250 °C at a rate 5.0 °C/min, held for 5.0 min, and finally raised to 300 °C at a rate of 7.0 °C/min. The temperature was also held for 5.0 min at 300 °C. The PAH compounds were identified using the NIST library search program, and the 16 U.S. EPA specified PAHs were confirmed and quantified using the retention times and calibration curves from the standard PAH compounds. During the analysis process, five fly ash samples were doped with a known amount of deuterated PAH compounds (naphthalene- d_8 , anthracence- d_{10} , and benz-[a]anthracene- d_{12}) before extraction to determine the recovery rate for the analysis process. A 96.2% recovery rate was achieved for the study. A high volatile bituminous coal, 10.5% ash, 34.6% volatile matter, 50.4% fixed carbon, and 5.2% hydrogen, was used in this study.

Results and Discussion

At the beginning of this study, the same sample was extracted, concentrated, and analyzed under the same conditions three times to determine the analysis system errors. The results indicate that the error range in this study is $\pm 5\%$. Three- and four-ring aromatic compounds were the major products from pyrolysis conditions, while naphthalene (two-rings) is the dominant PAH in fly ash collected from oxygen-rich combustion conditions. Only naphthalene was detected in the bed ash of the FBC system.

Lab-Scale FBC Reactor. The effects of pyrolysis temperature and excess air ratio were determined in a series of experiments. Approximately 40 different PAH compounds were identified with the GC/MS through the 60 000 compound NIST library search. However, only a few U.S. EPAspecified PAHs were confirmed, using the retention times from a PAH standard mixture, as listed in Table 1. Threeand four-ring aromatic compounds were the major PAHs in the fly ashes from the different experimental conditions. The total amount of PAHs obtained at 800 °C is almost twice that obtained at 900 °C using pyrolysis conditions. The higher temperature may provide more energy to break more bonds in the PAHs. This is also supported by the fact that no fivering compounds was determined when the temperature was increased to 900 °C. There was almost 80 times more PAHs produced at 800 °C than the PAHs extracted with solvents from the raw coal, as shown in Table 1. This suggests that the majority of PAHs are formed in breakdown reactions, with condensation and cyclization mechanisms playing less important roles.

In general, during coal combustion (even with an excess air ratio less than 1, partial thermal decomposition) the total amount of PAHs produced decreased with an increase in the level of excess air. The amount of PAHs produced dropped sharply after the excess air level was raised above 1. No significant difference is observed in the behavior of each aromatic ring compound; in each case the quantity of the PAHs that is observed in the reaction products decreases as excess air ratio increases. The results also suggest that incomplete combustion is the main reason for the emission of PAHs. The content of PAHs in the fly ashes (the minimum, at excess air ratio of 1.14) is seven times more than the PAHs extracted from the raw coal. This also indicates that the formation of PAHs is mainly through converting coal macromolecular aromatic structures into different size fragments and then decomposing and cracking the fragments into lower molecular weight PAHs under the FBC combustion

TABLE 1. U.S. EPA Specified PAHs Identified in the Ashes $[\mu g/(g \operatorname{ash})]$

	00	PF1	PF2	CF1	CF2	CF3				
PAHs in Fly Ash										
Two-Rings										
naphthalene	2.78	65.82	20.28	23.81	19.91	6.50				
Three-Rings										
acenaphthene acenaphthylene fluorene phenanthrene anthracene subtotal	1.36 b 1.46 b 2.82	4.18 75.21 48.02 60.04 27.03 214.48	2.30 b 27.14 42.11 15.39 86.94	b 76.42 54.89 70.02 31.39 232.72	b 15.01 13.80 30.08 15.02 73.91	<i>b</i> 3.53 2.39 6.01 2.51 14.44				
Four-Rings										
fluoranthene pyrene benzo[a]anthracene chrysene subtotal	b b b b	49.08 32.61 21.82 19.28 122.79	42.08 28.22 27.21 11.30 108.81	48.02 29.31 <i>b</i> 13.39 90.72	41.70 30.23 37.28 20.71 129.92	5.80 4.22 5.59 2.01 17.62				
benzo[<i>e</i>]pyrene totals	b 5.60	Five-Rin 36.20 439.29	n gs b 216.02	b 347.25	b 223.74	b 38.56				
PAHs in Bed Ash										
naphthalene		b	b	10.31	9.43	12.71				
^a OC – original coal: PE1 – 800 °C, pyrolysis: PE2 – 900 °C, pyrolysis:										

 a OC – original coal; PF1 – 800 °C, pyrolysis; PF2 – 900 °C, pyrolysis; CF1 – 800 °C, combustion, excess air ratio = 0.50; CF2 – 800 °C, combustion, excess air ratio = 1.00; CF3 – 800 °C, combustion, excess air ratio = 1.14. b Under the detection limit (0.1 ppb when the SIM mode is chosen).

conditions. In the oxygen-rich conditions, the PAHs will further undergo oxidation reactions and produce more carbon dioxide and water in the flue gas. However, if there is a lean oxygen condition in the fluidized bed combustor, more PAHs will be emitted with fly ashes.

Very small amounts of naphthalene was the only PAH identified in the bed ash, as shown in Table 1. This small amount may be due to the last second PAH products formed and surviving combustion before the furnace was turned off.

The results from the study of the gas phase PAHs in flue gas shows a different trend than with the PAHs in fly ash. The effects of pyrolysis temperature on PAHs in the gas-phase collected by the filter, condenser, and Tenax are listed in Table 2. Naphthalene was identified as the most prominent peak in the chromatograms when pyrolysis temperature was less 700 °C. The reason may be that naphthalene has the lowest boiling point among the PAHs and the highest stability, thus avoiding decomposition. With an increase in pyrolysis temperature, the amount of the smaller PAH molecules of PAH like naphthalene and fluorene decreased, while the emission of larger molecules increased with an increase in temperature. The minimum PAH emissions were produced around 600 °C. This may mean that both pathways of degradation of the coal matrix and the intermolecular cyclization from small species may occur above 400 °C for PAH formation in the flue gas under fuel-rich conditions. At the low temperature, the major pathway for PAH formation is degradation to emit smaller products during the devolatilization process. However, the effect of intermolecular cyclization becomes more and more important with an increase in the temperature, where large PAHs are produced from the combination of smaller PAHs. It is also possible that large PAHs are produced during the deep degradation of char.

The 0.1 MW_{th}**FBC System.** The FBC system with vortexing secondary air in the freeboard was used to conduct an experiment to determine the PAHs produced during combustion. From previous experiments run to study NO_x, SO_x,

TABLE 2. Amount (μ g/g Coal) of PAHs in the Coal and Collected by the Filter, Condenser, and Tenax in the Pyrolsis Process at Different Temperatures^a

		400 °C		500 °C		600 °C		700 °C		800 °C	
PAH	coal 97025	Α	В	Α	В	Α	В	Α	В	Α	В
Two-Rings											
naphthalene	1.34	1.10	0.22	1.26	0.31	0.63	0.40	0.39	0.45	0.16	0.85
				Thr	ee-Rings						
fluorene	0.13	0.29	0.03	0.80	0.61	0.33		0.28	0.66	0.30	0.79
anthracene	0.05	0.51	0.07			0.32	0.47	0.95	0.45	0.77	0.65
phenanthrene	0.07	0.77		1.10	0.16	0.37	0.30				
				Fou	ur-Rings						
chrysene		0.28	0.04	0.61	0.12	0.20	0.09	0.35	0.06	0.35	0.13
pyrene	0.01	0.12	0.03	0.32	0.04	0.22	0.15	0.43	0.22	0.53	0.27
subtotal	1.60	3.07	0.37	4.09	1.24	2.07	1.41	2.40	1.84	2.11	2.69
total			3.47		5.30		3.48		4.24		4.80

^a In the table, A represents the amount of PAHs collected by the filter and condenser, while B represents the amount collected with a Tenax trap.



FIGURE 2. The effect of combustion temperature on the number of fused rings in PAHs in the fly ash.

and HCl emissions, there was evidence that factors including temperature, excess air ratio, residence time (fluidizing velocity or bed height), and the secondary/primary air ratio greatly effected the amount of these compounds emitted during combustion.

During this study the temperature, excess air ratio, bed height, and secondary/primary air ratios and their effects on PAH formation and emission were examined. Each of these parameters was investigated independently in this study, since they can be controlled in different ways. The combustion efficiency for all tests was in the range of 98.5–99.5% with carbon content ranging in the fly ash from 15% to 5%.

From all test runs, incomplete combustion of coal is the main factor resulting in the emission of PAHs with the fly ash. The total amount of PAHs was much higher in the fly ash than in the bed ash. PAHs in quantifiable amounts were only found in the fly ash samples. The largest detectable PAHs were those with four fused rings, including fluoranthene and pyrene. No detectable amounts of PAHs were determined in the bed ash samples. The most probable explanation is that bed ash has a very long residence time (average 30–60 min) with high temperatures and undergoes thorough mixing and contact with the oxidant gas. All combustible compounds were burned before the bed ash was removed from the combustor. The average carbon content in bed ash is only

0.4% for the combustion runs in the WKU–FBC facility. Naphthalene was detected in every fly ash sample, while its content varied from 20 ng/(g ash) to 480 ng/(g ash), depending on the temperature, excess air ratio, and other factors. Upon comparison with the results [in the order of μ g/(g ash)] obtained from the lab-scale FBC reactor (without limestone fed), the PAH content in the fly ash from the bench-scale study is much less. The PAH content in the bench-scale is only in the order of ng/(g ash). The major reason for this behavior may be due to good solid and gas mixture and addition of limestone in the bench-scale FBC facility.

The combustion temperature has been found to be one of the most important factors affecting fossil fuel combustion in FBC systems, in which the burning speed of fuel is kinetically controlled due to high intensity turbulence between the solid and gas phases in the fluidizing condition. Higher combustion temperatures typically result in high degrees of burn-out in shorter times. In this study, high combustion efficiency (99.4%) was reached at high combustion temperature (882 °C), while 98.4% was obtained at 787 °C. The relationship between the PAH content in fly ash and combustion temperature is shown in Figure 2. An increase in combustion temperature causes a decrease in the PAH content in the fly ash. The PAH content decreased from 720 ng/(g ash) to 30 ng/(g ash) when the temperature was raised



FIGURE 3. The effect of excess air ratio on the number of fused rings in PAHs in the fly ash.

from 787 °C to 882 °C (static bed height = 0.65 m; excess air ratio = 1.25).

Considering the number of rings in the PAHs in the fly ash, the major reductions in PAH emissions occur for the two and three fused ring PAHs which are more completely combusted when the temperature is increased from 787 °C to 810 °C. The amount of four fused ring PAHs remained fairly constant in this temperature range. After the temperature is raised to 843 °C, no PAHs with more than three fused rings were found in this study. However, PAHs with two and three fused rings were still detected even at the highest temperature studied (882 °C). Considering another point, major compounds in three-rings PAHs at 843 °C are phenanthrene, acenaphthylene and anthracene. So, increases in the three-ring content in the fly ash may come from the decomposition of four-ring PAHs, such as pyrene or chrysene.

The excess air ratio is another important factor that influences the combustion of fossil fuels. In a series of tests, the combustion air flow rate (76 Nm³/h), bed temperature (810 °C), and bed height (0.67 m) were kept constant, and the excess air ratio was only adjusted by the coal feeding rate. Figure 3 shows the relationship between the PAH content in the fly ash and the excess air ratio. There is a direct relationship between PAH emissions and the excess air ratio, in that, as the amount of excess air is increased for the combustor, the PAH content in the fly ash decreases (combustion efficiency raised from 99.1% to 99.4%). With an increase in excess air, the amount of oxygen readily available to react also increases. When this occurs, the PAH fragments from the coal have the opportunity to react with the oxygen to form CO_2 and H_2O .

The number of rings in the PAHs in fly ash versus the excess air ratio illustrates that at the first step, large PAHs with three and four fused rings burned out with an increase in excess air ratio; at the second step, the excess air ratio is greater than 1.25, the major reduction in the total PAHs in fly ash occurs with naphthalene.

Fluidizing velocity is related to the erosion rate of metal in an FBC system. A small increase in fluidizing velocity will cause a severe erosion effect of particles on heat exchange tubes. Therefore, in the general operation of an FBC boiler, any load change of the boiler is achieved through adjusting the bed height (dense zone), with fluidizing velocity kept almost constant. In an FBC system, bed height represents a high solid density and a high turbulence zone in which heat exchange tubes are immersed, the temperature is uniform, and only a 10-20 °C difference exists in the entire space. Typically, 80-85% of the combustible coal is burned in this zone. In some ways, it also can represent the residence time of fuel particles inside the combustor. Usually, long residence times for particles can be reached at high bed heights when the fluidizing velocity is kept constant. The results of a study of bed height on the PAH content in fly ash at a bed temperature of 810 °C and excess air ratio of 1.25 is plotted in Figure 4. Compared to the results from the effects of combustion temperature and excess air ratio on the PAH content in the fly ash, the bed height showed the same general trend on PAH emissions. A very significant drop of PAH content in fly ash occurs with a bed height increase from 0.5 to 0.7 m (static condition), but no further decrease in PAH emissions occurred for bed heights more than 0.7 m. The final value for PAHs at 0.81 m bed height is 190 ng/(g ash), which is six times the final amount of combustion temperature effect. The PAHs with three fused rings was still detected at high percentages (\sim 50%) of the total PAHs at the 0.81 m static bed height. Thus, the results indicate the effects of combustion, excess air ratio, and bed height on PAH reduction in this study are in the following order: combustion temperature > excess air ratio > bed height.

The effect of particle size of fly ash on PAH content was also investigated in this study. The results are illustrated in Figure 5. The PAH content in the fine particle fly ash (Dp <0.10 mm) is five times higher than that in the coarse particle fly ash with (0.10 < Dp < 0.30 mm). The major reasons for this occurrence may be the combustor residence time for the fly ash and the surface area. The carbon content in the fine particle fly ash (17.2%) is higher than in the coarse particles (6.5%) in the WKU-FBC system. The coarse particle fly ash may fall near the wall of furnace, due to gravitational forces, to increase its residence time in the combustor, whereas the fine particle fly ash is lost from the combustor rapidly and has a short residence time. The fine particle fly ash has more surface area per unit mass than the coarse particles, thus more condensed PAHs can be absorbed as compared to absorption by the coarse particles. The results also suggest that the sampling system and methods should address the fine particle fly ash collection (such as the ash in the baghouse or the last stages of the electrostatic precipitator) in PAH studies with industrial boilers.



FIGURE 4. The effect of bed height on the PAH content in the fly ash.



Particle Size of Fly Ash

FIGURE 5. The effect of particle size on the PAH content in the fly ash.

It is known that air staging combustion can effectively control NO_x emission in the effluent gas during combustion processes. Up to 50% reduction of the NO concentration in the flue gas can be achieved at a secondary/primary air ratio of 30-50%. In some ways, air staging combustion technology can also improve SO_x capturing efficiency. An understanding of the role of air staging combustion on PAH emissions from FBC systems is not presently known. The effect of the secondary/primary air ratio on the PAH contents in fly ash is presented in Figure 6. The secondary air has a significant effect on the PAH emissions in fly ash. At a low location in the combustor (1.8 m from the distributor) and below the level of the secondary air nozzles, the fly ash (with 25.2% carbon content) collected with the secondary air on had a PAH content about fives times that in the fly ash sample (with 14.3% carbon content) collected without secondary air. However, at a high location (4.3 m above distributor, near the combustor exhaust), the PAH content in the fly ash sample with secondary air (4.8% carbon content) was only one-fourth that in the fly ash sample without secondary air (7.5% carbon content). Only naphthalene was detected in the 4.3 m samples with secondary air. In this series test, the total air flow (primary and secondary air) and coal feeding rate were kept constant. When a given secondary air flow was used, the primary air was reduced by the same volume. Thus, the actual excess air ratio in the fluidizing zone (below the level of secondary air nozzles) when air is being injected into the freeboard as secondary air is lower than that when secondary air is not being used. Low excess air ratios always cause high PAH emissions in the fly ash. Another factor to be considered for the high location (4.3 m) position is that the secondary air nozzles inject the air tangentially at an angle of 30 degrees into the freeboard to form a strong vortex flow. Under this tangential flow, particles escaping from the fluidized bed are separated from the flow. The large particles fall back into the bed along the wall, while the small particles form a suspended layer to prolong their residence time in the combustor. Thus, a more complete burn-out can be obtained with the tangential flow. Very low PAH contents were determined in the fly ash samples with the secondary air influence. As a consequence, high vortex secondary air (air staging) injected into the freeboard of the FBC system



FIGURE 6. The effect of secondary air on the PAH content in the fly ash.

is an effective method to minimize PAH emissions, along with the other benefits including reduction of NO_x and SO_x emissions. Fewer PAHs will be produced in fluidized bed combustion systems if the bed temperature and the excess air ratio are at optimal conditions.

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