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NITRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS
IN COAL COMBUSTORS AND EXHAUST STREAMS

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1. SUMMARY OF RESEARCH APPROACH

Nitro-polynuclear aromatic hydrocarbons (nitro-PAH) are the predominant mutagens on respirable particles from coal-fired boilers. Since nitro-PAH are not primary products of coal devolatilization, their formation must involve secondary chemistry at elevated temperatures. However, it is not known where in the combustion or exhaust processes they form, which reaction species are involved, or how concentrations are influenced by operating conditions. The objectives of this three-year project were to (1) identify the conditions which promote the nitration of PAH during primary combustion, reburning, hot gas cleanup, and particulate removal; and (2) investigate the potential relationship between NO_x abatement and PAH nitration.

Meeting the objectives of this program involved two broad tasks: (1) Preparing the polynuclear aromatic hydrocarbons (PAH) under closely monitored pulverized fuel (p. f.) firing conditions; and, (2) analyzing the PAH samples to monitor extents of nitration, ring number distribution, etc. While both activities were essential to this project, they involved completely separate scientific procedures and equipment. So in this, as in all previous reports, our findings are segregated according to their relation to either sample preparation or sample analysis. In actuality, Dr. Niksa and Prof. Hildemann each had a student working on these respective parts of this project.

A novel coal flow reactor burning actual coal products that operates over the domains of heating rates, temperatures, fuel-equivalence ratios, and residence times in utility boilers was used to generate the coal tar samples. The distribution of products obtained from primary, secondary, and oxidative pyrolysis of two coal types, Pittsburgh No. 8 and Dietz, were analyzed, with emphasis on the nitrogen-containing species generated.

The coal tar samples collected from the coal flow reactor were fractionated based on their size and polarity using gravity flow column chromatography. After examining how the sample fractionation depended on the coal type and pyrolysis conditions, the relatively nonpolar fraction was further analyzed via high performance liquid chromatography, to characterize the ring number distribution of the polycyclic aromatic compounds (PAC) present. Finally, gas chromatographic techniques were utilized to measure the amount of nitrogen-containing PAC present, and to investigate how much of these nitrogen-containing species consist of nitro-PAH.

2. FINDINGS

2.1 The Radiant Coal Flow Experiments

2.1.1. Coal Flow Reactor

A schematic of the radiant coal flow reactor appears in Figure 1. Briefly, pulverized particles are fed into an entrainment stream, forming an optically-thin suspension which flows downward into the radiant furnace. Near-black-body thermal emission from the graphite in the furnace rapidly heats the particles as they traverse the furnace. The entrainment air remains relatively cool and quenches chemistry among the primary products as they are expelled, allowing samples to be collected that are representative of primary devolatilization. For secondary pyrolysis, the suspension loading is increased to enhance interphase heat transfer and raise the gas temperature; in addition, residence times are extended by using a longer furnace. For oxidative pyrolysis, oxygen is added to the process stream upstream of the furnace section.

Product recovery and analysis begins at the furnace outlet, where a quench nozzle blasts argon into the process stream, rapidly quenching all chemistry and nucleating the tar into an aerosol. Products are segregated into bulk solid particles, tar/soot aerosol, and noncondensable gases. The tar/soot and char particles are separately collected and weighed. Then the tar is separated from the soot via sonication of the sample in tetrahydrofuran (THF). The noncondensable gases are quantified by non-dispersive infrared and chemiluminescence analyzers, and via gas chromatography. Carbon, hydrogen, and nitrogen contents of condensed products are determined, with mass balances that close to within 5% in individual runs.

2.1.2. Experimental Results

Ultimate analyses for the Dietz and Pittsburgh No. 8 coals were performed. As shown in Table 1, Dietz, a subbituminous B coal, has a high oxygen content, while Pittsburgh No. 8, a high volatile bituminous coal, has a relatively low oxygen content. Coal tar samples were generated that ranged from the onset of secondary pyrolysis, where little or no soot was generated, through the late stages of secondary pyrolysis, when soot production was high.

Fig. 1. The radiant coal flow reactor.

Table 1. Coal and Tar Samples Studied

Coal Rank Low High

Coal Type:	Subbituminous			High-Volatile Bituminous		
	Dietz			Pittsburgh #8		
	wt%			wt%		
	Volatile Matter	O	C	Volatile Matter	O	C
	39.9	24.1	69.5	34.7	8.5	82.5

Pyrolysis Conditions:

Pyrolysis Conditions	Soot Production	Pyrolysis Conditions	Soot Production
Temperature - Central velocity - Voltage	(wt% of dry ash free)	Temperature - Central Velocity - Voltage	(wt% of dry ash free)
1386 - .18 - 21	1.44	1378 -.33 - 27	0.00
1386 -.18 - 25	3.32	1358 -.18 - 21	5.15
1485 -.18 - 77	5.16	1474 -.18 - 77	9.44
1651 -.18 - 77	8.32	1660 -.18 - 77	22.50
1640 -.18 - 77	10.20		

Figure 2 shows the total weight loss and aerosol yield versus furnace temperature for Pittsburgh No. 8 under secondary pyrolysis conditions. While the combined yields of tar plus soot (seen as aerosol yield) remain constant, but the detailed product distributions indicate that soot and tar cannot be exchanging quantitatively, due to radical differences in their elemental compositions. As shown in Figure 2, furnace temperature can be viewed as a measure of the extent of secondary pyrolysis — soot percentages increase from 30% to more than 80% for the range of experiments conducted for this Pittsburgh coal.

Experiments were also conducted under oxidative pyrolysis conditions. As shown in Figure 3a for the Dietz coal, as the oxygen level increases from 2% to 17%, the weight loss increases, due to char combustion. The aerosol yield falls from 16 to 8 wt. %, indicating that soot oxidation is far from complete. Similar results were obtained for the Pittsburgh No. 8 coal, as shown in Figure 3b.

The amount of tar formed in these experiments is far too little for analysis via chromatographic procedures. The tar yield is below 4 wt. % for the Dietz, and below 2 wt. % for the Pitts. No. 8, and shows no dependence on the oxygen level. The minimal tar yields, even at low oxygen levels, indicates that the furnace temperature being utilized is hot enough to sustain nearly complete secondary pyrolysis.

The measurements of the major combustion products (Figure 4) for both coals show that CO_2 yields increase monotonically with increasing oxygen, while H_2O yields seem to approach an asymptote. The observed decrease in CO and hydrogen with increasing oxygen concentrations is a result of the impetus to maintain water gas shift equilibrium as the stream temperature becomes hotter.

The measurements of the hydrocarbon products, shown in Figure 5, indicate that the combustion times for the gaseous volatiles are considerably faster than those for the solid products, as expected. However, the persistence of the hydrocarbons is somewhat surprising. Although the oils are rapidly eliminated, methane and acetylene persist long beyond the point where enough oxygen is present to burn out all the volatiles.

This persistence of hydrocarbons exerts a significant impact on the conversion of nitrogen species, which is illustrated in Figure 6. As the oxygen level increases, the char-N falls, which is indicative of the consumption of char by combustion. The level of HCN also falls, as does the nitrogen content of the aerosol products. The impact of the persistence in hydrocarbons is seen mainly in the behavior of NO: as long as hydrocarbons are present,

Figure 1(a) Weight loss at 300 (∇) and 1200 #/cm³ (o) and the respective aerosol yields ($\bullet$) throughout secondary pyrolysis of Pit. #8 coal.

Figure 2(b) Soot percentages in the aerosol from Pit #8 coal at 300 (+) and 1200 (x) #/cm³.

Dietz, Major Products

Figure 3a. Weight loss (○), tar yield (▽), soot yield (▼), and tar + soot yield (●) from Dietz subbituminous coal at various O₂ levels in a 1700° K furnace.

Figure 3b. Pit. #8, Major Products

Dietz, Major Gaseous Products

Figure 4a. Yields of CO₂ (○), H₂O (▽), CO (●), and H₂ (▼) (on a scale of 10× sensitivity) during oxidative pyrolysis of Dietz coal.

Figure 4b Pit. #8, Major Gaseous Products

Dietz, Hydrocarbon Gases

Figure 5a. Yields of C_2H_2 (●), CH_4 (▼), and oils (○) from Dietz coal.

Figure 5b. Pit. #8, Hydrocarbon Gases

Dietz, Fuel-N Distribution

Figure 6a. Distribution of the Dietz nitrogen among char (∇), HCN ($\bullet$), tar + soot ($\circ$), NH₃ ($\blacksquare$), and NO ($\blacktriangledown$).

Figure 6b. Pit. #8, Fuel-N Distribution

the NO conversion efficiency is low. Once an oxygen level of greater than 10% is reached, there is nearly complete conversion of HCN, char-N, and soot-N to NO. This reflects the fact that there are no longer hydrocarbons present that can reduce the NO into N₂. While H₂ and CO remain at high oxygen levels, these cannot serve as effective NO reductants.

2.2 Coal Tar Characterization

2.2.1. Gravity Flow Column Chromatography

This chromatographic procedure, shown in Figure 7, utilizes two modules in series. The first module, containing a particle sorbent material, is utilized for sample loading. The second module, where the fractionation takes place, is packed with cyano-bonded packing material. A sample is fractionated by first loading onto the first module, and then passing through successive aliquots of solvents to elute the various fractions. By ordering the elution solvents to go from nonpolar to highly polar solvents, fractionation on the basis of polarity is achieved.

Figure 8 illustrates the fractionation procedure for a Pitts. No. 8 coal tar sample. A series of 5 solvents are utilized; by adding THF as the final, most highly polar solvent, recoveries of greater than 90% are typically achieved. As is shown in Figure 9, The PAC species of greatest interest for this study will elute primarily in the toluene fraction, with some of the highly-substituted (more polar) PAC eluting in the dichloromethane (DCM) fraction.

In Table 2, the average fractionation and recoveries are shown for the coals under a range of pyrolysis conditions. It is noteworthy that the Dietz coal tar generated during the early stages of secondary pyrolysis contains a substantial amount of polar material that eluted in the methanol fraction. This is likely due to the much larger amount of oxygen present in the Dietz coal itself. However, as secondary pyrolysis proceeds, the amount of polar compounds in the tar samples from both coals decreases.

Figure 10 shows more clearly the trends measured in the coal tar fractionation characteristics. As the soot yield increases, the concentration of almost every fraction decreases. It is noteworthy that the toluene fraction remains the largest of the solvent fractions throughout the range of secondary pyrolysis conditions studied, for both coals. Since the toluene fraction contains 2- to 6-ring PAH, along with monosubstituted PAH,

Sample preparation

Fractionation

Figure 7. Gravity-flow Column Chromatography System

Figure 8. Fractionation and recovery of a 20.56 mg sample of Pittsburgh #8 coal tar, using improved prefractionation scheme.

Figure 9. Fractionation of 1474 K Pittsburgh #8 coal tar samples

Table 2. Polarity Distributions via Gravity-Flow Chromatography for both Dietz and Pittsburgh #8 Coal Tars

Coal tars	Yield (%)			Yield (%)				
	Soot Pyrolysis condition	Char	Gas	Non-polar → Polar				
				Heptane (2.5 ml)	Toluene (9 ml)	Dichloromethane (8 ml)	Methanol (6 ml)	Tetrahydrofuran (8 ml)
<u>Dietz</u>	1.44 1386-18-21	54.53	31.69	0.43	5.29*	2.10	2.94	1.59
	3.32 1386-18-25	45.33	31.79	0.04	5.64*	1.52	1.49	1.53
	5.16 1485-18-77	45.33	41.68	0.05	4.50	1.32	0.98	0.98
	8.32 1651-18-77	37.57	50.05	0.28	2.78	0.43	0.21	0.37
	10.20 1640-18-77	42.55	45.1	0.05	1.47	0.24#	0.15#	0.18
<u>Pittsburgh #8</u>	0.00 1378-33-27	89.69	4.24	0.3	3.64*	0.78	0.76	0.60
	5.15 1358-18-21	60.04	19.98	0.16	7.86	2.43	1.44	2.94
	9.44 1474-18-77	57.61	19.58	0.01	7.34	2.35	1.18	2.49
	22.5 1660-18-77	49.76	24.5	0.02	2.12	0.44#	0.27#	0.40

* - Estimated proportions; # - collected by 7 ml and 4 ml of DCM and MeOH, respectively.

Figure 10a. Polarity distribution via gravity-flow chromatography for Dietz coal tars

Figure 10b. Polarity distribution via gravity-flow chromatography for Pittsburgh #8 coal tars

and the potential health effects of 4- and 5-ring PAH are of greatest concern, this fraction is of greatest interest to this study.

In Figure 10a, it is seen that the toluene fraction initially increases during the early stages of secondary pyrolysis for the Dietz coal. It is known that the extent of coal oxidation during pyrolysis greatly depends on the coal rank: the higher the oxygen content in the coal, the more substantial the decrease in organic emissions. Therefore, it is not surprising that, during the early stages of secondary pyrolysis, the more-polar compounds present in the DCM and methanol fractions of the Dietz coal tar convert into less-polar PAH eluting in the toluene fraction.

It should be noted that the loss of mass in the solvent fractions for Dietz coal tars exceed the mass increase observed for soot. In contrast, the total mass loss from the solvent fractions for Pittsburgh No. 8 coal tar is insufficient to account for the increase in soot yield. This is relevant for considering the possible routes for soot formation. It has been proposed that soot could be formed either through direct conversion of tars/oils, or via production from volatile hydrocarbons. The measurements here suggest that the soot from Dietz coal could originate mainly from tar compounds, while soot formed from Pitts. No. 8 coal may originate from volatile hydrocarbon precursors.

2.2.2. High Pressure Liquid Chromatography

A range of operating conditions were examined for HPLC analysis, as shown in Figure 11. To obtain good sensitivity for a range of PAC ring sizes, a broad wavelength interval was chosen (220–340 nm). Selection of the solvent used for sample preparation and the mobile phase utilized in the column was based on optimization of peak resolution. Utilization of methanol as the preparation solvent and a mixture of 98% heptane/2% DCM as the eluent composition gave narrow peaks with good separation.

Based on the utilization of standard mixtures, it was verified that the non-substituted PAH did, indeed, elute according to fused ring number. Figure 12 shows the calibration curve obtained for the HPLC column, while Figure 13 illustrates the segregation of the non-polar PAC from those having polar substituents. It is interesting to note that the separation depends on fused ring numbers, not the total number of rings: for example, rubrene elutes with other 4-ring PAC, even though it consists of 4 fused rings plus another 4 aromatic rings that are separated from the fused structure. Based on analyses with standards, it appears that non-polar PAC having up to 5 fused rings will reliably segregate

**Wavelength intervals
(nm)**

252-256

220-340

260-340

260-380

Solvent of sample preparation

THF¹

MeOH²

**Mobile phase
(Isocratic)**

Hexane + THF(%)

100

97.5 2.5

Heptane + THF (%)

100

97.5 2.5

Heptane + DCM³(%)

97.5 2.5

98 2

99 1

1. Tetrahydrofuran
2. Methanol
3. Dichloromethane

Figure II, Optimization of HPLC operating conditions.

Elution Volume (ml), V_e

Figure 12.

HPLC calibration curve obtained with a mobile phase of 98% heptane and 2% dichloromethane at flowrate of 1 ml/min

Figure 13. Elution order of substituted PAH

both from each other, and from PAC having polar substituents. Therefore, ring number distributions for the various coal tar samples were only analyzed up through 5-ring PACs.

The results of HPLC analyses performed for the toluene fraction of the coal tar samples are given in Table 3. Each of the measurements represents a mean of three analyses, and the samples are listed in order of increasing extent of secondary pyrolysis. Analogous to what was presented for the GFCC analyses, the trends in ring numbers observed via HPLC for each of the coals are plotted in Figure 14.

While the trends in ring number concentrations seen for the Pittsburgh No. 8 mirror those seen for the toluene fraction as a whole, a much more complicated behavior is observed for the Dietz coal tar toluene fraction. It is noteworthy that the 2- and 3-ring PAH in both coals are depleted more drastically as secondary pyrolysis proceeds than the 4- and 5-ring PAH. By the end of secondary pyrolysis, the toluene fraction of both the Dietz and Pitts. No. 8 coal tars contain almost identical proportions of the 2- to 5-ring PAH. This indicates that the influence of the original coal structure on the coal tar products becomes minimal by the end of secondary pyrolysis.

2.2.3. Comparison of GFCC and HPLC Results

To more closely compare the polarity and ring number distributions of the two coal types, a different measure of the extent of pyrolysis was utilized. Since the sum of soot plus tar (that is, the total carbonaceous aerosol) remains invariant throughout secondary pyrolysis, the soot fraction (that is, the fraction of the total carbonaceous aerosol consisting of soot) was utilized as a basis for comparison.

In Figure 15, the polarity characteristics of the two coals are compared. In the early stages of secondary pyrolysis, it is clear that some of the compounds in the Dietz coal tar transform from being highly polar to less polar in character: the DCM and methanol fractions decrease while the toluene fraction increases. The trends observed for the Dietz coal tar imply that, in the early stages of secondary pyrolysis, the larger and/or more polar PAC originally present cleave into smaller, less-polar PAC. For Pittsburgh #8 coal tar, no comparable trend is evident: all of the fractions simultaneously decrease once the soot fraction (SF) goes beyond 26%.

A similar analysis can be conducted for the ring number distribution characteristics of the two coal tars. As shown in Figure 16a, there is again the suggestion for Dietz coal

Table 3. PAH Ring Number Distribution for Dietz and Pittsburgh #8 Coal Tars

Coal tars	Soot yield (%) Pyrolysis condition	% of total emissions consisting of			
		<u>PAH ring groups</u>			
		2-3 rings	4 rings	5 rings	
<u>Dietz</u>	1.44 1386-18-21	0.270	0.064	nm	
	3.32 1386-18-25	0.178	0.054	0.014	
	5.16 1485-18-77	0.432	0.293	0.142	
	8.32 1631-18-77	0.151	0.338	0.080	
	10.20 1640-18-77	0.063	0.143	0.095	
<u>Pittsburgh #8</u>	0.00 1378-33-27	0.168	0.055	nm	
	5.15 1358-18-21	0.701	0.349	0.070	
	9.44 1474-18-77	0.628	0.365	0.140	
	22.5 1660-18-77	0.059	0.149	0.094

Figure 14a. Ring number distribution via HPLC for Dietz coal tars

Figure 14b. Ring number distribution via HPLC for Pittsburgh #8 coal tars

Percentage of Total Emissions

Figure 15. Polarity Distribution for both Dietz and Pittsburgh #8 Coal Tars

Percentage of Total Emissions

Figure 16, Ring-Number Distribution for Both Dietz and Pittsburgh #8 Coal Tars

that substituted PAH (which are not shown in the plot) are transforming between SF of 25% and 40% into nonsubstituted PAH. For the Pitts. No. 8 coal, shown in Figure 16b, the amounts of 2-5-ring PAH decrease even though the total toluene fraction increases. This suggests that this increase in the toluene fraction must be due to the formation of substituted PAH.

2.2.4. Gas Chromatography with Chemiluminescence Detection

Due to time and budgetary constraints, this project was only able to perform a preliminary examination of the coal tar samples via GC with chemiluminescence detection. This initial effort was aimed at examining the total nitrogen content of the toluene fraction. As shown in Figures 17 and 18, no N-PAH were detected during the early stages of secondary pyrolysis. As secondary pyrolysis became more severe, more N-PAH peaks appeared. Because the total nitrogen content in coal tars decreases as secondary pyrolysis proceeds, the trends observed here are not indicative of the total nitrogen content in the coal tars. Instead, the N-PAH trends observed could be due to the cleavage of aliphatic C—C or C—O bonds as secondary pyrolysis proceeds, releasing smaller N-containing aromatics from the organic matrix.

Figure 17. GC/Chemiluminescence Measurement for Dietz Coal Tars.

Figure 18. GC/Chemiluminescence Measurement for Pittsburgh #8 Coal Tars.

3. FUTURE PLANS

While the end date for this project has passed, work on analyzing and interpreting the data continues. Three papers are in various stages of preparation: one dealing with the pyrolysis product analyses, a second examining the GFCC results, and a third analyzing the HPLC and GC results.