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NITRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS
IN COAL COMBUSTORS AND EXHAUST STREAMS

Quarterly Report for the
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1. SUMMARY

During the period October 1, 1993 to December 31, 1993, the PAH preparation project at SRI International and the development of analytical methods for PAH proceeded smoothly without any major obstacles. Activity during this quarter focused on validating the performance of the PAH preparation facility against past results from the radiant coal flow experiment for secondary coal volatiles pyrolysis, now that all laboratory facilities used to prepare PAH for this project have been restored to working condition at SRI International. Dr. Cho first ran numerous tests with coal to qualify his experimental techniques against our current database. The data show the correct qualitative features, very good reproducibility, and good consistency with past results. The ultimate yield for primary devolatilization is not achieved at 1380 K, but an asymptotic value of 50 wt. % is observed at all higher temperatures. This value is reproduced to within about 2 wt. %. Also, the sum of the yields of tar and soot is constant at all temperatures, as it should be because it is invariant throughout secondary pyrolysis. Finally, the soot fraction increases monotonically for hotter furnace temperatures, but in a surprisingly nonlinear way at low temperatures.

Work also continued this quarter on optimizing the HPLC analysis procedures to give reproducible, quantitative results for the PAH ring number distribution. Substantial improvement in analytical performance has been obtained by installing a new chromatographic column, and further improvements have resulted from modifying the eluent composition and sample preparation procedures. Utilizing this improved analytical method, a preliminary calibration curve for the ring number distribution of 3- to 6-ring PAH has been obtained.

2. INTRODUCTION TO THE PROGRAM

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. Results from this study will help to relate the environmental impact of mutagenic emissions to boiler firing strategies.

The objectives of this three-year project are 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. A novel coal flow reactor burning actual coal products operates over the domains of heating rates, temperatures, fuel-equivalence ratios, and residence times in utility boilers. A fluidized bed will be built for studies of simulated hot gas cleanup at lower temperatures. Gas chromatography with chemiluminescence detection will measure the aggregate amount of nitro groups present, to determine when nitro-PAH first appear, and how nitration is affected by the operating conditions. Tars from primary and secondary pyrolysis and oxidative pyrolysis will be fractionated into chain hydrocarbons, polynuclear aromatics, oxygenated species, and a basic fraction, so that their ring number distribution can be monitored with high performance liquid chromatography.

3. FINDINGS

3.1 Introduction

Meeting the objective of this program involves 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 distributions, etc. While both activities are essential to this project, they involve scientific principles which are almost completely unrelated. So in this and all future reports, our findings will be segregated according to their relation to either sample preparation or sample analysis. In actuality, Dr. Niksa and Prof. Hildemann each have an associate working on these respective parts of this project.

Regarding activity on the PAH preparation side of the project, our technical progress has resumed completely. All of the laboratory facilities are operating in Dr. Niksa's new laboratory at SRI International. Data is presented below that demonstrates the satisfactory performance of the overhauled induction power supply for the radiant coal flow experiment and the redesigned coal feeder. All the analytical equipment is also fully operational, now that the gas chromatograph has been calibrated for the light hydrocarbons of interest. We did, however, decide to monitor most permanent gases with on FTIR spectroscopy, because the on-line detector for water could not be restored to good working order without a major (and expensive) overhaul. This upgrade will continue into the next quarter.

To continue optimizing the operating parameters used in high performance liquid chromatography (HPLC) for separating polycyclic aromatic hydrocarbons (PAH) according to the fused aromatic ring numbers, different compositions of eluent were examined this quarter. A new analytical column installed in HPLC also was tested by

injecting the same standard compounds as used last quarter. The column evaluation, streamlined operating conditions, and a preliminary calibration curve for HPLC separation are discussed below.

3.2 Sample Preparation

Activity during this quarter focused on validating the performance of the PAH preparation facility against past results from the radiant coal flow experiment for secondary coal volatiles pyrolysis, now that all laboratory facilities used to prepare PAH for this project have been restored to working condition at SRI International. Dr. Cho first ran numerous tests with coal to qualify his experimental techniques against our current database. This experiment requires an operator with considerable manual dexterity to regulate the variable pressure drop across the filters in the centripeter as they accumulate tar during the course of an experiment.

The results in Fig. 1a show that Dr. Cho has mastered this experiment. Fig. 1a shows our latest data on total weight loss, the sum of tar and soot aerosol, and the mass fraction of the aerosol which is tar, based on solubility in tetrahydrofuran (THF). The experimental conditions are for controlled secondary volatiles pyrolysis, in which higher furnace temperatures achieve higher extents of conversion of tar into soot. All runs were taken with the same nominal transport velocity, but the actual transit time of coal through the reactor decreases at hotter temperatures, from about 175 to 150 ms, because of the greater thermal expansion of the hotter flow. The loading used in all cases with furnace temperatures hotter than 1500 K is $1200 \text{ \#/cm}^3$, the same as we used in all previous experiments on secondary pyrolysis. A loading one-fourth as large was used at 1380 K, in a marginally successful attempt to achieve complete primary devolatilization with little or no secondary pyrolysis with the current furnace configuration. (All prior primary

Figure 1. Secondary pyrolysis of Dietz subbituminous coal: (a) results of current coal tar generation experiments; and (b) results of previous experiments, for comparison.

devolatilization studies were conducted in a 5 cm flow tube, not the current 15 cm flow tube.)

The data show the correct qualitative features, very good reproducibility, and good consistency with past results. The ultimate yield for primary devolatilization is not achieved at 1380 K, but an asymptotic value of 50 wt. % is observed at all higher temperatures. This value is reproduced to within about 2 wt. %. Also, the sum of the yields of tar and soot is constant at all temperatures, as it should be because it is invariant throughout secondary pyrolysis. Finally, the soot fraction increases monotonically for hotter furnace temperatures, but in a surprisingly nonlinear way at low temperatures.

For sake of comparison, our past results for secondary pyrolysis of a similar but not identical coal appear in Fig. 1b. Note that the coolest temperature in this study is 1480 K, 100 K hotter than in previous work. For this reason, the ultimate primary devolatilization yield is observed at all temperatures. However, the older value is about 10 wt. % greater than the current value. We believe that this is due to different coal properties, as follows: The ultimate analysis of the Dietz coal used in the older work is 69.5 daf wt. % C, 5.0% H, 1.0 % N, 0.4 % S, and 24.1 % O. That for the DECS 9 from the current work is 75.5 % C, 5.2 % H, 0.9 % N, 0.4 % S, and 17.9 % O. Two very substantial differences between these analyses explain the lower yields from the DECS 9 sample: its much higher carbon content (75.5 vs. 69.5%) and its much lower oxygen content (17.9 vs. 24.1%).

In a comparison of the aerosol product yields in Figs. 1a and b, it appears that the one from the DEC 9 is lower by about 3 wt. %. However, the older work monitored and included an oils yield of 3-4 wt. % into the aerosol yield, but oils were not observed in the recent work. Finally, the observed soot fractions are the same in both cases, except that the new value at 1750 K is 10 % greater than the old value.

Regarding analytical equipment, new calibration curves were acquired for C₂ through C₆ hydrocarbons with the refurbished GC in our lab. This supplements and completes the prior calibrations of CO, CO₂, O₂, NO, CH₄, and C₃H₈. All of the calibration cases and final operating conditions are collected in Table I. The only other instrument needed to close C/H/N balances over the observed products from individual runs is an on-line non-dispersive IR (NDIR) detector for water vapor. Unfortunately, we found out that a major and expensive overhaul is required to restore it. Instead, we have begun to set up our FTIR as an on-line monitor for selected noncondensable products from the radiant coal flow experiment. It should be fully operational next quarter.

3.3 Sample Analysis

3.3.1. Eluent Composition Tests

The HPLC results from last quarter showed very broad peaks for the 6-ring PAH, despite testing a variety of eluent compositions under isocratic conditions. It was suspected that the 6-ring PAH were not fully dissolving, even in the 80% heptane/20% tetrahydrofuran (THF) eluent mixture. Hence, some variable eluent compositions were tested this quarter, in which the proportion of solvent THF was gradually increased to enhance the ability of the eluent to dissolve 6-ring PAH.

Figure 2 shows the chromatograms obtained by running two gradient flows. The eluent in Figure 2a was programmed to use 97.5% heptane and 2.5% THF for the first 4 minutes, followed by increasing the THF to 40% over a one minute time period, and then holding the new composition of 60% heptane and 40% THF for an additional

Table I. Calibration Data for the Refurbished Gas Chromatograph

species	method	T _{oven} , °C	carrier cc/min	injection	ranges ppm	calibration curves ¹	
						A	B
H ₂	TCD	90	Ar/10	syringe(1cc)	10-10 ⁶	0.11460	0.9964
N ₂	TCD	-60	He/10	MPV(3:1)	50-10 ⁴	0.03923	1.2328
O ₂	TCD	-60	He/10	MPV(3:1)	50-10 ⁴	0.17320	1.1071
CO ₂	TCD	90	Ar/10	syringe(1cc)	10 ² -10 ⁵	0.72820	1.0239
CH ₄	FID	120 to 220 ²	Ar/30	MPV(3:1)	10-10 ⁴	0.10563	1.0320
C ₂ H ₂	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.14079	0.9373
C ₂ H ₄	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.08246	1.0023
C ₂ H ₆	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.05695	1.0278
C ₃ H ₆	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.06438	1.0030
C ₃ H ₈	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.04048	1.0327
C ₄ H ₈	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.05058	1.0027
C ₅ H ₁₀	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.04059	1.0018
C ₆ H ₁₂	FID	120 to 220	Ar/30	MPV(3:1)	10-10 ⁴	0.03045	1.0197

Note:

1. The form of calibration curves is [ppm]=A[area]^B.
2. The temperature programming is at 100 °C for 5 min, ramp to 200 °C by 20 °C/min, 200 °C for 4 min, ramp to 220 °C by 10 °C/min, and 220 °C for 30 min, resulting in the total analysis time of 45 min including C₆ species.

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Figure 2. HPLC chromatograms for 16-PAH standard using the DNAP column under variable eluent composition conditions, starting with heptane/THF at a ratio of 97.5/2.5% for the first four minutes: (a) THF fraction increased from 2.5% to 40% over a one-minute period; and (b) THF fraction first increased to 25%, and then later increased to 50% (see text for details).

25 minutes. Figure 2b shows the chromatogram obtained from (i) starting with 97.5% heptane and 2.5% THF for the first 4 minutes; (ii) then increasing the THF to 25% over a one minute time period; (iii) holding at this composition for 15 minutes; (iv) increasing the proportion of THF to 50% over another one minute interval; and (v) finally holding at this composition for another 10 minutes. Although this resulted in improved peak resolution (e.g., the peak at 10.7 min in Figure 2a was resolved into 2 peaks in Figure 2b), peak broadening remained a problem, particularly for the 6-ring PAH. In addition, the extent of baseline drift observed in Figure 2 was quite high. These observations suggested that the DNAP column was not suitable for analyzing complicated mixtures, even though it has shown excellent resolution for very simple PAH mixtures.

3.3.2. Selection and Characterization of New Column

Another column with a bonded phase of cyano (CN) was purchased from Alltech. This simpler bonded phase was expected to allow a more complete elution of complex PAH mixtures. In addition to the column change, a new deuterium lamp was installed in the detector, to increase the sensitivity in measuring absorbance.

The CN column selected has the same size characteristics as the DNAP column: as shown in Table II, it is 25 cm x 4.6 mm, made of stainless steel, and contains a particle size of 5 μ m and a pore diameter of 6 nm. To optimize the operating parameters for the new CN column, various wavelength intervals and eluent compositions were tested by injecting the standard mixture composed of 16 PAH. Figure 3 shows the four wavelength intervals and different eluent compositions tested using CN column. In order to detect the absorbance of various sizes of PAH, ranging from 2 to 10 aromatic rings, the wavelength channel from 220 to 340 nm was selected as the optimal detection range; not surprisingly, this is quite similar to the 220-380 nm bandwidth previously selected for the DNAP

Table II. Comparison of HPLC Column Attributes

	<u>DNAP Column</u>	<u>CN Column</u>
<u>Bonded phase</u>	Dinitroanilino Propyl	Cyano
	$\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	Si-CN
<u>Company</u>	ES Industry	Alltech
<u>Column size</u>	25 cm x 4.6 mm (stainless steel)	
<u>Particle size</u>		5 μ
<u>Pore size</u>		6 nm
<u>Phase</u>		Normal

Figure 3. Optimization of HPLC operating conditions.

column. Selecting a lower wavelength of 220 nm ensures that small PAH such as naphthalene will be detected, while the high end of the wavelength range will allow detection of the larger PAH. The absorbance detected from the other 3 wavelength ranges shown in Figure 3 will also be stored for reference purposes.

The eluent composition also was reexamined using the new CN column. As shown in Figure 3, three types of comparisons were made. First, heptane and hexane were compared as the primary component of the mobile phase mixture, then THF and DCM were compared as the secondary component of the solvent mixture, and finally, various isocratic mixtures of heptane and DCM were tested. As Figure 3 shows, the optimal eluent composition was determined to be 98% heptane and 2% DCM. This mobile phase mixture resulted in narrow peaks with good peak separations. Additional tests also determined that preparing the sample for analysis in methanol, rather than THF, further improved the quality of the elution peaks obtained for the 6-ring PAH.

As shown in Figure 4, the refinements described above result in much narrower peak widths, especially for the 6-ring PAH. In addition, the CN column eluted the 16 PAH compounds in less than 7 minutes, which is roughly one-third of the time required using the DNAP column. Thus, the CN column will subsequently be utilized in the HPLC to separate the complex coal tar mixtures of interest in this project.

3.3.3 Ring Number Distributions

The HPLC chromatogram shown in Figure 4 shows eleven separate peaks, which were obtained from injecting the mixture consisting of 16 PAH compounds. This is not surprising, because we expected that PAH containing the same number of fused aromatic rings would either coelute or elute within a narrow range of time. This is also consistent

Figure 4. HPLC chromatogram for 16-PAH standard mixture using the CN column [98% heptane + 2% dichloromethane, 1 ml/min flowrate, 260-340 nm wavelength interval].

with the main purpose of HPLC separation in this project: we want to quantify PAH according to their ring numbers, not identify each individual compound in the coal tar samples.

The elution trend of PAH, based on the standard mixture shown in Figure 4, can be summarized as follows: the 2- and 3-ring PAH elute after 3.843 minutes, while 4-, 5-, and 6-ring PAH are eluted after 4.654, 5.579, and 5.898 minutes, respectively. A preliminary calibration curve was established on the basis of elution volume (V_e) and ring number (n), which is shown in Figure 5. The preliminary calibration equation demonstrates an empirical quadratic relationship between V_e and n as follows:

$$V_e = -0.534 + 1.816n - 0.123n^2$$

It should be noted that a final calibration curve will be determined to quantify the full ring number range of aromatic compounds in coal tar samples; this preliminary one is only applicable for characterizing PAH with less than or equal to 6 rings. Further work will include optimizing and refining the calibration curve by injecting PAH containing more than 7 aromatic rings, as well as evaluating the elution behavior of PAH standards containing substituents.

4. Short Term Goals

During the coming quarter, we will resume PAH sample collection. Our first experiments on oxidative pyrolysis will be conducted, first to prepare a suite of PAH samples, then to monitor all major products of oxidative pyrolysis. Experiments on oxidative pyrolysis conditions supplement our existing data on primary devolatilization and secondary pyrolysis. Early in the quarter, Dr. Cho will define the operating conditions with various oxygen levels. Then he will acquire the samples for controlled oxidative pyrolysis of 3 or 4 coal types. Time permitting, he will also begin to monitor

Elution volume (ml), V_e

Figure 5. Preliminary calibration curve showing relationship between elution order and PAH ring number.

all gases present in significant quantities with FTIR to close the elemental balances in his datasets.

From the work done this quarter, we have found that the resolution of 16 PAH standards via HPLC is very sensitive to the solvent used to prepare the injection samples. Although methanol has been found to be more suitable than THF for preparing injection samples, one more solvent will be tested next quarter: decahydronaphthalene (Lafleur et al., 1987).

After evaluating the merits of using decahydronaphthalene, standard mixtures containing larger PAH (composed of more than 6 aromatic rings) and PAH containing substituents will be purchased and injected next quarter. This will allow refinement of the preliminary calibration curve, and also will enable us to examine how the substituents alter the elution time of saturated PAH containing a given number of rings. Finally, the toluene fractions from a variety of coal tars, produced from burning Pittsburgh #8 and Dietz coals, will quantitatively be characterized via HPLC based on the finalized calibration curve.

5. Reference

Lafleur, A.L., Monchamp, P.A., Plummer E. F., Wornat, M.J., "Universal Calibration Method for the Determination of Polycyclic Aromatic Hydrocarbons by High Performance Liquid Chromatography with Broadband Diode-Array Detection", Analytical Letters, 20 (8), 1171-1192 (1987).

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