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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 July 1, 1992 to September 30, 1992 our environmental impact statement was approved, and DOE funds have been released for this project. The technical projects are proceeding smoothly without any major obstacles.

Regarding PAH preparation, our efforts this quarter were directed at preparing PAH samples at well-controlled extents of secondary pyrolysis. The same operating conditions used in the past were implemented this quarter to prepare PAH samples at well-controlled extents of secondary pyrolysis from a Pit. #8 hvA bituminous coal. The new data are in excellent agreement with the old. Both ultimate yield values and soot percentages at particular furnace temperatures from these data sets are within experimental uncertainties. PAH samples have now been prepared to cover extents of conversion of coal tar into soot from 35 to 80 %. Additional runs during primary devolatilization have yielded PAH samples that cover nearly the full range of this process as well. Hence, all PAH samples from the Pit. #8 coal sample are in hand. We also began to collect the analogous PAH samples from a subbituminous coal this quarter.

This quarter's efforts at sample analysis focused on testing and modification of the gravity-flow column chromatography procedure using actual tar samples. Extra samples collected during combustion experiments using the Pit. #8 bituminous coal were used to refine the preseparation technique. Solvent volumes were adjusted to optimize sample separation, and additional tests were conducted to determine the reproducibility of the fractionation and recovery. Further refinement in the experimental methodology allowed 80% recovery of the coal tar samples to be reproducibly achieved.

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, Profs. Niksa and Hildemann each have a student working on these respective parts of this project.

Regarding PAH preparation, our efforts from July through September 1992 were directed at preparing PAH at well-defined extents of secondary pyrolysis. The same operating conditions in the longer furnace used in previous work in this lab yielded the same satisfactory results. Results presented below characterize the transient evolution of the last noncondensable species of primary devolatilization as well as the conversion of tar into soot during secondary pyrolysis. Weight loss and tar yields as well as the percentage of soot in the aerosol products throughout primary devolatilization and secondary pyrolysis for Pit. #8 coal are collected in this report.

The analytical efforts this quarter were aimed at refining the sample prefractionation procedure using actual coal tar samples. The results presented in section 3.3 describe modifications that enabled us to consistently achieve 80% recovery of the coal tar samples. The manner in which a coal tar sample fractionates represents a bulk characterization that can be compared with other coal tar samples as both a function of combustion conditions and of the type of coal used.

3.2 Sample Preparation

3.2.1 Operating Conditions for Secondary Pyrolysis Studies

In any practical application, the products of primary devolatilization are radically transformed by secondary chemistry after they escape into the gas phase. Heavy, aromatic coal tars are especially susceptible to sooting, which has important practical consequences. Soot forms luminous mantles around burning coal particles that emit radiation very effectively. Sooting also releases substantial amounts of H_2 from soot precursors and aliphatic hydrocarbons, which accelerates burning velocities during combustion and raises the heating values of gasification products. Oxygenated aromatics expel CO and azaarenes expel HCN during secondary pyrolysis. Secondary pyrolysis also expels and transforms noxious heteroatomic compounds, and creates organic mutagens. All of these features are evident in studies in the literature, including earlier studies from this laboratory.

The same radiant coal flow reactor described in our first and second quarterly reports is also used for secondary pyrolysis studies. Only one operating condition is adjusted to promote secondary chemistry: The coal loading at the inlet is quadrupled to roughly $1200 \text{ \#/cm}^3$, which imparts similar heating rates and ultimate temperatures to the suspension and its entrainment stream because higher loadings increase the interfacial area for their convective heat transfer. As in the primary devolatilization studies, the length of the hot zone is 12.5 cm. The entrainment gas velocity is fixed at 18 cm/s in all cases.

In this operating mode, the severity of the thermal processing is regulated simply by increasing the furnace temperature in successive runs with the same inlet gas velocity and suspension loading. The thermal histories among such cases have similar heating rates and reaction times but different ultimate temperatures. The suspension initially heats faster than the

gas, but the high convective heat transfer rate quickly brings the particle and gas heating rates into balance at nominal values of 104 K/s. As a result, the temperature difference is less than 200 K at the outlet of the 1740 K furnace. Calculated thermal histories for all conditions in our secondary pyrolysis studies were presented in our first quarterly report.

Ultimate suspension temperatures are usually much hotter in this operating mode than in the primary devolatilization studies. According to the simulations, the suspension reaches 1000 K at the least severe secondary pyrolysis condition of flow through the furnace at 1480 K in 175 ms. At the most severe condition the maximum suspension temperature is 1350 K. Gas temperatures exceed 1200 K at the most severe conditions.

Since the same conditions are used for secondary pyrolysis studies in this project as in our past work, the residence times measured previously can be applied to the new dataset. Nominal particle residence times in the radiant coal flow experiment are set by the inlet gas flowrate and the furnace length. But nominal values are roughly twice those determined by direct measurements under experimental conditions for several reasons. Boundary layers grow on the tube walls, contracting the cross section of the potential core which carries the suspension, and accelerating it. As the gas heats, its expansion accelerates the flow. The inertia of the suspension, coupled through drag, also accelerates the flow.

Measured residence times are assigned as the time interval between the interruption of two HeNe laser beams 0.75 cm beyond the endplates of the furnace by the leading edge of a long pulse of fuel suspension. Measured residence times for furnace temperatures from 1480 to 1740 K range from 175 to 155 ms, decreasing with increasing wall temperature due to the thermal expansion of the entrainment stream.

Past data from primary devolatilization and secondary pyrolysis studies in this lab show that the presence of soot is a definitive indicator for the extent of secondary pyrolysis. Soot yields are based on solubility in tetrahydrofuran (THF), and the scheme for product recovery and separation that was described in our third quarterly report.

3.2.2 Experimental Results

All experiments were run with the Pit. #8 hvA bituminous sample that we obtained from PETC for previous studies. Its label is PSOC-1451D and its ultimate analysis is 82.5 dry-ash-free (daf) wt.% C; 5.6 % H; 1.8 % N; 1.6 % S; and 8.5 % O (by diff.). On a dry basis it has 12.6 % ash.

The data covering secondary pyrolysis for the Pit. #8 appear in Figs. 1 and 2. Total weight loss and aerosol yields are plotted versus furnace temperature in Fig. 1, and the weight percentages of soot in the aerosol appear in Fig. 2. The total weight loss in Fig. 1 reaches an ultimate value of 60 daf wt. % at furnace temperatures hotter than 1550 K. This value is within experimental uncertainty of our previous value of 61 wt. % for the same coal. At 1480 K, the former value of weight loss was also below the ultimate value, as observed again in this dataset. This is simply an indication that the reaction conditions are not severe enough at both lower furnace temperatures to complete the later stages of noncondensibles evolution from primary devolatilization, when substantial additional amounts of CH₄ and CO are expelled. Weight loss values are presented for two loadings, 300 and 1200 #/cm³. Conversions at the lower loading tend to be slightly greater than those for denser suspensions. This may seem to be contrary to the influence of loading on the interphase heat transfer (discussed above), which would elevate temperatures for the higher loading, and thereby increase the ultimate yields. However, loading exerts the opposite effect on residence time: Denser suspensions move faster through the furnace by virtue of greater drag, so

Figure 1. Weight loss at 300 (▽) and 1200 #/cm³ (○) and the respective aerosol yields (▼,●) throughout secondary pyrolysis of Pit. #8 coal.

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

their residence times are shorter. Apparently, this is the major factor that reconciles the lower yields for higher loadings in Fig. 1.

The combined yields of tar plus soot, seen as the aerosol yields in Fig. 1, remain constant throughout secondary pyrolysis. The invariant value of 23 wt. % is within experimental uncertainty of the ultimate tar yield from the primary devolatilization studies (in the third quarterly report). However, our former value was much higher, at 36 wt. %, because it also included the oils yield. The earlier data does show that oil yields remain the same until the very latest stages of secondary pyrolysis, consistent with invariant sums of the yields of tar and soot.

These data as well as others in the recent literature establish that the sum of the yields of tar and soot is invariant throughout secondary pyrolysis, but our detailed product distributions showed that the obvious interpretation is incorrect. Soot and tar cannot be exchanging quantitatively because their elemental compositions are radically different. The atomic C/H ratio of coal-derived soot covers the same range as in flames, from about 2 to 10, and soot contains no oxygen. Tar C/H ratios can be less than one, and O/C ratios can reach 0.5. Throughout secondary pyrolysis tar compositions change as substantial amounts of oxygen and hydrogen are expelled as CO and H₂, respectively. The elimination of CO from tar is compensated for by addition of C₂H₂, so aggregate yields of the heavy products remain invariant.

While aggregate yields of tar and soot remain the same, the soot percentages in the aerosol cover a wide range as furnace temperatures are increased from 1380 to 1660 K. Observed values for two loadings appear in Fig. 2. For the complete range of operating conditions, they grow from 30 % at 1380 K to more than 80 % at 1660 K. Thus, these experiments have generated PAH at well-controlled extents of secondary pyrolysis that cover virtually the entire process. The furnace temperature could be raised, although the amount of PAH in the aerosol for soot fractions above 0.8 is too small to conveniently analyze.

At fixed loading, the soot percentage is near-linearly proportional to furnace temperature. Consequently, furnace temperature is a convenient scale for the extent of secondary pyrolysis in this dataset. It seems that soot percentage is more sensitive to furnace temperature at the higher loading, although the scatter among the low-loading data obscures this trend somewhat. This trend is easy to rationalize. At higher suspension loadings, there is more soot in the suspension near the furnace outlet. While the entrainment gas is transparent to the furnace radiation, soot is not. So higher soot loadings elevate the suspension and gas temperatures at the furnace outlet, increasing the rates of secondary pyrolysis and the soot fractions in the aerosol.

All of the data for primary devolatilization and secondary pyrolysis of Pit. #8 coal are collected in Tables 1 and 2. This dataset is complete, and all of the required PAH samples from this sample have been acquired. During the quarter, several runs were made with a Dietz subbituminous coal. The complete dataset for this sample will be reported in the next quarterly report.

3.3 Sample Analysis

During the furnace experiments generating the Pit#8 coal tar, several sizable duplicate samples were collected and saved for analytical calibration purposes. Some of these samples were utilized this quarter towards refining the calibration of the gravity-flow column chromatographic system. Besides finalizing the selection of the solvent volumes to be used for the prefractionation procedure (as discussed in Section 3.3.1), these samples were also used for the purpose of identifying strategies for increasing the sample recovery (as discussed in Section 3.3.2).

TABLE 1. PRODUCT YIELDS FROM PRIMARY PYROLYSIS OF PITTSBURGH #8 BITUMINOUS COAL FOR 300#/CM³ INLET LOADING WITH THE FURNACE AT 1380K.

Entrainment Velocity, m/s	Tar	Soot	Char
1	0.6	nm	95.6
	1.3	nm	95.5
0.5	1.6	0.00	91.0
	1.7	0.00	90.2
	1.7	nm	95.9
	1.7	nm	93.0
0.33	6.6	nm	89.9
	7.3	nm	nm
	8.3	nm	89.9
	6.1	0.00	89.7
	3.8	0.00	nm
	6.7	0.00	86.8
0.25	9.4	nm	82.9
0.18	18.1	nm	65.1
	18.3	3.4	nm
	19.1	2.1	58.0
	19.9	0.8	60.4
	17.8	0.3	60.8

TABLE 2. PRODUCT YIELDS FROM SECONDARY PYROLYSIS OF PITTSBURGH #8 BITUMINOUS COAL AT 18 CM/S INLET GAS VELOCITY, DRY-ASH-FREE (DAF) WT. %.

Loading #/cm ³	Wall Temp., K	Tar	Soot	Char
300	1380	13.2	6.5	62.4
		11.5	7.9	61.9
	1485	14.4	7.5	51.3
		17.6	6.6	53.0
	1580	10.9	12.6	46.9
		9.9	15.5	49.5
1200	1475	14.6	5.4	56.8
		13.4	9.4	57.6
		14.2	6.2	55.6
	1580	7.5	14.8	52.1
		7.6	16.5	52.8
	1660	5.6	17.0	45.2
		nm	nm	57.7
		3.2	22.5	49.8

3.3.1 Prefractionation Procedure

As described in the previous quarterly report, initial calibration of the gravity-flow column chromatograph was performed using standard compounds. Since coal tar contains a mixture of hundreds to thousands of organic compounds, further testing and refinement of the prefractionation procedure using actual coal tar was necessary. The approach taken was identical to what was done for the initial calibration using the standards. Several aliquots (0.5-2 ml apiece) of each of the 4 solvents were sequentially loaded onto the column and collected in separate vials. Based on the amount of sample recovered in each vial, the optimal quantity of each solvent was determined. The sum of the amounts of sample contained in each vial was used to determine the overall recovery.

The major refinement resulting from this series of experiments was to reduce the volume of heptane used from 3 ml to 2.5 ml. The shape of the recovery curve obtained for heptane suggested that some higher molecular weight compounds were eluting in the last 0.5 ml of heptane added. The heptane volume was reduced to assure that the majority of the low-ring-number PAH would elute later, in the toluene fraction, rather than earlier in the heptane solvent, since we will be focusing on the heptane and dichloromethane fractions for subsequent analyses.

3.3.2 Sample Fractionation and Recovery

As mentioned in our last quarterly report, recoveries of 67 to 100% were obtained for samples of pure organic species. Using the Pit #8 coal, many replicate prefractionations were performed in which specific steps were varied, one at a time, in an effort to identify those steps strongly influencing the amount and reproducibility of the overall sample recovery. As a result of these experiments, the step in which the samples in the vials were dried prior to weighing was determined to contribute greatly to the reproducibility of the results. Additional safeguards were added to ensure better uniformity in the drying procedure.

Using Pit #8 coal tar, the gravity-flow column chromatograph was able to reproducibly recover about 80% of the sample. As shown in Figure 3, over half of the recovered mass eluted in toluene and about one-third eluted in the more-polar dichloromethane, with the remainder eluting in the highly-polar methanol that is used as the final solvent. Each point in Figure 3 represents a separate vial of eluant collected, illustrating that recoveries using each solvent decrease noticeably as the volume of solvent increases. This indicates that an optimal volume of each solvent is being used.

The finding that a large fraction of the Pit #8 coal tar is relatively nonpolar is not surprising, given that it is a high-volatile bituminous coal. The quantification shown in Fig. 3 of the amounts of polar vs. nonpolar organics eluting will provide a useful comparison with other coals to be tested which are expected to have a much higher fraction of polar organics (e.g., Lower Kittanning, a low-volatile bituminous). It will also be possible to determine the extent to which this fractionation varies with the combustion conditions.

4. SHORT RANGE OBJECTIVES

During the coming quarter, Mr. Dadamio will continue to prepare PAH samples at controlled extents of primary devolatilization and secondary pyrolysis for various coal types. Once he has finished with the subbituminous sample, he will move on to a low volatile bituminous sample and an Ill. #6 sample.

Over the next three months, Ms. Yu will examine the effect of starting sample size on the fractionation and recovery of coal tar. Using the duplicate Pit #8 samples, she will determine the range of starting sample sizes for which results are the same. She will also try an alternative method of drying the fractionated samples in an effort to streamline the prefractionation procedure.

Gravity-flow Column Chromatography
Coal Tar: Pitz-1474-0.18-84

Figure 3. Fractionation and recovery of Pitz #8 coal tar using gravity-flow column chromatography.

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