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NITRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS
IN COAL COMBUSTORS AND EXHAUST STREAMS

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1. SUMMARY

During the period January 1, 1993 to March 31, 1993, the development of analytical methods for PAH proceeded smoothly without any major obstacles, but the PAH preparation project was temporarily suspended because Dr. Niksa left Stanford to join the staff at SRI International. Approval by DOE of a revised budget for this grant allowed funds to be subcontracted to SRI for Dr. Niksa's continued involvement. All of his laboratory facilities associated with this project were moved during the quarter, and the major utilities for the high temperature furnaces were installed in the new lab. By the end of the quarter, some of the major analytical instruments were already being reactivated, although the PAH preparation facility will not be fully operational again until well into the coming quarter.

For sample analysis, research this quarter continued to focus on finalizing the prefractionation methodology. Sample sizes ranging between 10 and 20 mg were determined to give acceptably accurate mass recoveries after the gravity flow column chromatographic separation. Further tests were conducted aimed at refining the volumes of solvents to be used. In addition, the fractionation of coal tar samples from Dietz, Pittsburgh #8, and Lower Kittanning coals were contrasted, and each was compared with the characteristics of the unburnt coal.

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.

One major institutional change occurred during this quarter. Dr. Niksa left Stanford to join SRI International as a Senior Chemical Engineer. He will be able to continue working on his part of this project because all of his laboratory facilities are moving with him to SRI, and funds for his continuing involvement were subcontracted to him at SRI, through a revision to the budget for this grant. However, Dr. Niksa's former research associate, John Dadamio, will remain at Stanford to pursue his Ph. D. on another research project. He will be replaced by Mr. Sunghwan Cho, a more advanced Ph. D. student who has worked with Dr. Niksa over the past 6 years. While Mr. Cho expects to complete his Ph. D. program at Stanford very shortly, he will continue working on this project as a post-doctoral associate, under the direction of Dr. Niksa. Mr. Cho also has very extensive experience with all of the instruments in this laboratory, including the operating procedures for the radiant coal flow experiment.

For refinement of the prefractionation procedure, smaller amounts of coal tars were analyzed this quarter, enabling a final determination of the proper range of sample sizes to be made. A fixed

set of solvent volumes was used to preseparate two more types of coal tars, a subbituminous coal, Dietz, and low-volatile bituminous coal, lower-Kittaning, in addition to Pittsburgh #8. The proportion of coal tar mass recovered in each fraction for these coal tars is presented and discussed below.

3.2 Sample Preparation

3.2.1 Relocation to SRI International

All of the laboratory facilities used to prepare PAH in this project were moved into 2 laboratories at SRI International. All of the equipment was relocated without incident or damage. These laboratories were already equipped with fume hoods, adequate ventilation, and the common laboratory utilities. However, additional power at 440 V was installed for the induction power supply in the radiant coal flow experiment.

Reconstruction is proceeding smoothly. The FTIR for product analysis has already been resurrected, and major elements of the furnace system have already been rebuilt. The entire system should be operating again late in the next quarter.

3.3 Sample Analysis

3.3.1. Prefractionation Procedure

To compare the proportions recovered for various coal tars and combustion conditions, identical solvent volumes must be used for the prefractionation of each coal tar sample. Based on the shape of the mass elution curves measured last quarter, smaller amounts of dichloromethane (DCM), 3 ml, and methanol, 4 ml, were tested this quarter to recover 7- to 10-ring polynuclear

aromatic compounds (PAC) and very polar polynuclear aromatic hydrocarbons (PAH), respectively (see Figure 1). As a result, the recovery of Pittsburgh #8 coal tar using 3 ml of DCM (instead of 7 ml used previously) dropped to 21% (from 28%), while the total fraction recovered by THF went up to 19% (from 14%). Not surprisingly, the higher DCM and methanol volumes are causing compounds to elute earlier than they would have otherwise. Because high temperature combustion conditions tend to generate coal tars containing large proportions of non-polar organics, and because various coals are expected to have different polarity distributions, different types of tar samples produced at higher temperatures will be tested to finalize the volumes used for each the solvents, including DCM. The shape of the elution curves measured for these tar samples will allow us to determine the minimum volume of each solvent sufficient to elute the bulk of elutable mass for that fraction.

Figure 1 summarizes the average fractionation characteristics of tar samples generated from Pittsburgh #8 coal at 1474°K. The average proportion of each fraction recovered by heptane, toluene, DCM, methanol, and tetrahydrofuran (THF) was 2%, 34%, 19%, 25%, and 6%, respectively. An additional 8 % of the total sample mass was recovered from the filtration and fractionation columns after adding the first 3 ml of THF. The total recovery of Pittsburgh #8 coal tar ranged from 84% to 94%, which is consistent with the results of Lafleur et al^[1]. Although tentative compound classes for the first four fractions are shown in Figure 1, based on work reported by Lafleur et al.^[2], further pre separation and high performance liquid chromatography (HPLC) analysis of standard compounds will be needed to conclusively identify the compound classes eluting in each fraction for our column and elution conditions.

3.3.2. Sample Recovery and Prefractionation

Efforts this quarter were aimed at determining a lower limit for sample mass based on measurement of recovery. Table 1 lists the total recoveries of various sample sizes of tar from

Figure 1. Fractionation of 1474 K Pittsburgh #8 coal tar samples

Table 1. Total recovery of Pittsburgh #8 coal tar (from combustion at 1474-0.18-84)
as a function of starting sample size.

Sample size (mg)	Total Recovery	Standard deviation *
20.56	0.87	0.02
14.27	0.95	0.02
14.27	0.90	0.03
11.28	1.05	0.05
8.23	1.16	0.02
7.23	1.08	0.07
5.05	0.94	0.04

* This standard deviation represents the accumulated error for replicate weighings of each fraction.

Pittsburgh #8 coal. Although 94% recovery of the smallest sample mass tested this quarter, 5.05 mg, was highly satisfactory, the total recoveries measured for a range of sample sizes, as shown in Table 1, suggest 10 mg as the minimum sample mass loaded in order to minimize the effect of absolute errors produced during the preseparation procedure on the accuracy of total recovery. The unusually high recovery obtained for the 8 mg sample suggests that sample sizes this small can result in less than accurate quantification of total recovery. Last quarter, 20 mg was determined to be the maximum sample size for preseparation of tar, based mainly on the duration of the gravity-flow column chromatographic procedure. Hence, the appropriate sample mass loaded should range from 10 to 20 mg for our gravity-flow column chromatography set-up.

In addition to the coal tars of Pittsburgh #8 tested over the past several quarters, the tar samples of subbituminous coal, Dietz, and low-volatile bituminous coal, lower-Kittanning, were also preseparated by the gravity-flow column chromatograph this quarter. Table 2 provides a comparison of the preseparation results for the three types of coal tars. These coal tars were generated under similar burning conditions (the first number in the code appearing under the coal types denotes the combustion temperature), and prefractionated using the same volumes of solvents, so that the polarity distributions of various coal tars can be compared based on the proportions recovered for each fraction. The first column lists the solvent volumes used: 2.5 ml for heptane, 5 ml for toluene, 3 ml for DCM, 4 ml for methanol, and 3 ml for THF. The recoveries of the heptane fraction show that the coal tars of lower-Kittanning contain the least amount of aliphatic compounds, which is expected since this low-volatile bituminous coal is well graphitized. It is also not surprising that toluene fraction collected the largest proportion of tar mass from lower-Kittanning among the three types of coal tars, because the original coal structures of lower-Kittanning coal contain very low concentration of oxygen and are broken into small fragments of neutral PAC during the burning process; these neutral organics are easily eluted by toluene. The fact that the methanol fraction recovered the largest portion of tar mass for the Dietz coal shows that this subbituminous coal generated more polar compounds in the tar samples,

Table 2. Average fractionation and recoveries for eluted tar samples from Dietz, Pittsburgh #8, and lower-Kittaning coals

Solvent (volume used)	Dietz 1371-0.33-27	Pittsburgh #8 1474-0.18-84	lower-Kittaning 1368-0.18-25
Heptane (2.5 ml)	0.03	0.02	0.01
Toluene (5 ml)	0.28	0.32	0.40
DCM (3 ml)	0.17	0.21	0.15
Methanol (4 ml)	0.36	0.26	0.20
THF (3 ml)	0.08	0.08	0.08
THF.Frc. ^a (3 ml)	0.04	0.07	0.07
THF.Fil. ^b (2 ml)	0.04	0.04	0.09

a. THF.Frc. represents the proportion of tar mass retained in fractionation column, which was eluted by 3 ml THF.

b. THF.Fil. represents the proportion of tar mass retained in filtration column, which was eluted by 2 ml THF.

which is also expected because of the high oxygen content in the original coal structure. Because the polarity distributions measured this quarter agree with the features of original coal structures, focusing in future work on characterizing in detail the coal tars of Pittsburgh #8 and Dietz coal will provide sufficient information to predict the characteristics of lower-Kittanning coal as well. Moreover, the fact that about 50% or more of the sample mass was recovered by the first three fractions (2.5 ml heptane, 5 ml toluene, and 3 ml DCM) suggests that these tar samples contain sufficient amounts of neutral compounds to characterize the fused ring-number distributions of polynuclear aromatic compounds by HPLC in the future.

4. SHORT RANGE OBJECTIVES

During the coming quarter, reconstruction of the radiant coal flow experiment should be completed, and Mr. Cho will begin to qualify his experimental techniques against our current database.

To optimize the solvent volumes for the fractions of toluene and DCM, the tar samples of Pittsburgh #8 and Dietz coal burned at higher temperatures (1640°K and 1660°K, respectively) will be analyzed in the upcoming quarter by the gravity-flow column chromatography. Then, the solvent volume to be used for each fraction will be finalized; this optimized procedure will be used in the future to prefractionate tar samples produced under the whole range of combustion conditions. In addition, Miss Yu will begin to select the proper column for HPLC analysis for studying the ring-number distributions of tar compounds.

5. REFERENCES

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