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NITRATION OF POLYNUYCLEAR AROMATIC HYDROCARBONS IN COAL COMBUSTORS AND EXHAUST STREAMS

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1. SUMMARY

Still pending approval of our environmental impact statement and release of funds for this project, we have continued moving forward with contingency financial backing from the Mechanical and Civil Engineering Departments at Stanford. During the period January 1, 1992 to March 31, 1992 both graduate students began to become familiar with their laboratory systems.

Regarding PAH preparation, our efforts this quarter were directed at identifying the operating conditions in the laboratory furnace that clearly resolve primary devolatilization from secondary pyrolysis. In previous studies, pristine tars from primary devolatilization were prepared in the radiant coal flow experiment with a furnace length of only 5 cm. Tars at various extents of secondary pyrolysis were generated in a hot-zone of 12.5 cm. For this project we decided to try to prepare both kinds of PAH in the 12.5 cm hot zone.

Preliminary screening surveys showed that, among the three possible ways to compensate for the longer furnace tube, only lowering the furnace temperature is really effective. Lowering the loading from its already low value of 300 #/cm³ is inconsequential, and raising the gas velocity to lower residence times in the longer hot zones causes deposition problems. The coal jet undergoes the transition to turbulence in less than 12 cm for entrainment velocities greater than 1 cm/s. By the end of the quarter, it was clear that the best value for primary devolatilization studies will fall within the range of 1150 to 1400 K. But at present we are still not completely satisfied with the resolution of primary devolatilization. As intended, the tars collected at short residence times are completely soluble in tetrahydrofuran (THF), indicating that no soot is present so no secondary pyrolysis has occurred. But at residence times long enough to attain ultimate primary devolatilization yields, some soot is present. We will make our final choice early in the next quarter, then begin to collect an inventory of primary devolatilization tars for subsequent detailed characterization.

Regarding PAH analysis, this quarter's activities were aimed at selecting and assembling the components comprising a gravity-flow column chromatograph, which will be used to fractionate the coal tar samples according to the polarity and molecular weight of the organic compounds. Based on a literature review, a packing material was selected for the column, along with the suite of solvents to be utilized for the fractionation procedure. In addition, assembly of the chromatographic system was nearly completed.

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 January through March 1992 were directed at identifying the operating conditions in the laboratory furnace that clearly resolve primary devolatilization from secondary pyrolysis. In previous studies, pristine tars from primary devolatilization were prepared in the radiant coal flow experiment with a furnace length of only 5 cm. Tars at various extents of secondary pyrolysis were generated in a hot-zone of 12.5 cm. For this study we decided to try to prepare both kinds of PAH in the 12.5 cm hot zone. Section 3.2 of the report describes the new operating conditions and presents conversion data and soot percentages to validate the resolution of primary and secondary pyrolysis at the new conditions.

For sample preparation, the first quarter of 1992 was spent selecting, procuring and assembling the gravity-flow column chromatograph. Section 3.3 in this report contains the details regarding this portion of the analytical method development.

3.2 Sample Preparation

3.2.1 Operating Conditions for Primary and Secondary Coal Tars

Primary devolatilization products are the gases created by chemistry among species and functional groups in the condensed phase only. Secondary products are formed from subsequent transformation among primary products after they pass through the interface between solid and gas. Coal devolatilization products are radically transformed by secondary pyrolysis as tars are converted into soot while oxygenated aromatics expel CO and azaarenes expel HCN.

Distinguishing primary devolatilization and secondary pyrolysis is largely a matter of independently regulating the thermal histories of suspended coal and its entrainment stream. Our first quarterly report described the operating principles of the radiant coal flow experiment, and showed data that documents how this system enables very close control over the extent of primary devolatilization and secondary pyrolysis. For studies of primary devolatilization, residence times are varied at fixed furnace temperature by adjusting the flowrate of the entrainment gas. Thermal histories in a series of runs have nearly the same heating rate, but the suspension achieves different temperatures at the outlet in each case. Higher temperatures are achieved as residence times are extended, but outlet temperatures of the coal particles are always well below the furnace temperature. Even so, progressively greater extents of devolatilization are achieved as the residence time is extended, and the particles are heated to higher temperatures. To study secondary pyrolysis, the entrainment gas flowrate is fixed while furnace temperatures are increased. The thermal histories among such cases have similar heating rates and reaction times but different ultimate temperatures. Extents of secondary pyrolysis increase as the temperature is raised. Calculated thermal histories for primary and secondary pyrolysis studies were presented in our first quarterly report.

In previous studies the length of the furnace hot-zone was also different for primary and secondary pyrolysis studies to accommodate the relatively short reaction time scales for transient primary devolatilization and the much longer reaction times for secondary pyrolysis. It was 5 cm for primary devolatilization but 12.5 cm for secondary pyrolysis studies. Largely for the sake of convenience, we decided to conduct both primary and secondary pyrolysis experiments (and future runs for oxidative pyrolysis) in the longer hot zone. The same conditions used in the past for secondary pyrolysis experiments will be reproduced, so previous characterizations of residence times, appropriate coal loadings, and gas flowrates remain valid. But new operating conditions had to be identified for the primary devolatilization studies.

Increasing the length of the hot zone increases the severity of conditions in the furnace. Obviously, the longer residence times in a longer furnace can be compensated for by increasing the gas flowrates. However, the relationship between residence time and entrainment gas flowrates is surprisingly complicated. Nominal residence times are roughly twice those determined by direct measurements under experimental conditions for several reasons. Boundary layers grow on 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.

However, as the gas flowrate is increased to compensate for the longer furnace, the coal suspension goes unstable and becomes turbulent in a shorter distance. This instability threshold limits the range of entrainment gas flowrates because turbulent coal jets expel tars and soot onto the quartz flow channel. As a carbonaceous layer accumulates, it absorbs radiation, and eventually heats the flow tube to its failure point.

There is another strategy for regulating the thermal histories in this furnace. The coal loading in this system directly affects rates of heat transfer between the suspension and its entrainment gas. First of all, the entrainment gases are transparent to radiation, so their only mechanism for heating is convection from the quartz tube walls and interphase heat transfer from hot particles in the suspension. Increasing the loading increases the interfacial area available for interphase heat transfer, which brings the thermal histories of gases and particles into line. Another way to compensate for the longer hot zone in our primary devolatilization studies is to decrease the loading, to keep the gas cooler and also to keep the particles cooler as they pass through the furnace.

The third and final strategy for compensating for the longer furnace tube is to lower the temperature in the radiant zone. Lowering the furnace temperature decreases the radiant flux onto the suspension, so the particles attain a specified temperature over a longer distance. Since furnace temperature is fixed in all runs to prepare primary devolatilization products, this strategy is implemented simply by identifying the lower furnace temperature that completely resolves primary devolatilization from secondary pyrolysis.

3.2.2 Experimental Results

All three strategies to identify new operating conditions for the primary devolatilization experiments were evaluated in runs during this quarter. Preliminary studies were first aimed at validating the methodology of John Dadamio, the new student on this project, against data acquired by more experienced operators in the past. Although all of the experienced operators have left Stanford, they were generously available for phone consultations. This exercise progressed as very specific aspects of the experimental method were recognized and perfected. Eventually, Mr. Dadamio's data drew within experimental uncertainty of Mr. Craig Castagnoli's for identical conditions.

Preliminary screening surveys also showed that, among the three possible ways to compensate for the longer furnace tube, only lowering the furnace temperature is really effective. In the previous primary devolatilization studies in the shorter hot zone, the loading was only 300 #/cm³. This level is already so low that heat transfer between the suspension and its entrainment gas is very slow; calculations estimate temperature differences at the outlet up to 500 K for this loading. Consequently, lowering the loading further could not compensate for the longer hot zone.

Instabilities in the coal suspension limited the maximum inlet velocity of the entrainment gas to only 1 cm/s. This value is actually only half of the maximum feasible value for the shorter hot zone. As explained above, the coal jet undergoes the transition to turbulence at shorter distances as the gas flowrate is increased. Unfortunately, the transition occurs in less than 12 cm for entrainment velocities greater than 1 cm/s.

By the end of the quarter, various furnace temperatures had been examined. It is clear that the best value for primary devolatilization studies will fall within the range of 1150 to 1400 K. But at present, we are still not completely satisfied with the results. As intended, the tars collected at short residence times are completely soluble in tetrahydrofuran (THF), indicating that no soot is present so no secondary pyrolysis has occurred. But at residence times long enough to attain ultimate primary devolatilization yields, some soot is present. We will make our final choice early in the next quarter, then begin to collect an inventory of primary devolatilization tars for subsequent detailed characterization.

3.3 Sample Analysis

3.3.1 Prefractionation Procedure

The tar sample collected from each radiant coal flow experiment will contain hundreds of organic compounds, ranging from low to high molecular weights, and from neutral to extremely polar. The chemical characteristics of each sample will be influenced both by the actual coal combustion conditions, and by the type of coal burned.

Because the ring number distribution of the PAH present in the tar samples is of interest, analysis via HPLC will be performed. It is known that polar compounds interfere with this analysis (Wornat, 1988, 1991); hence, a prefractionation procedure will be necessary as an initial step to separate the polar organics from the neutral material.

Gravity-flow column chromatography with the sequential use of four solvents (ranging from nonpolar to highly polar) has been successfully used to separate neutral PAH from the more polar species in a coal tar (Lafleur et al., 1988). As a result of examination of this and other literature, hexane, toluene, dichloromethane and methanol were selected (in order of increasing polarity) as the suite of solvents to be used. A cyano-bonded packing material was selected for the fractionation column, also based on a literature review.

Procurement and assembly of the gravity-flow column chromatograph was completed during the first quarter of 1992. As shown in Figure 1, the assembly consists of two modules in series.

The first module, containing a particle sorbent material, is utilized for sample loading. The sample, dissolved in tetrahydrofuran, is loaded onto the sorbent, and the solvent is allowed to evaporate. Then the solvent module is attached to the fractionation column, which is packed with cyano-bonded packing material. Successive aliquots of solvents are passed through this assembly, allowing fractionation of the sample on the basis of polarity and molecular weight.

Sample preparation

Fractionation

Figure 1. Gravity-flow Column Chromatography System

4. SHORT RANGE OBJECTIVES

During the coming quarter, Mr. Dadamio will identify the best temperature for primary devolatilization studies, then begin to accumulate PAH samples at prescribed extents of primary devolatilization. Time permitting, he will also validate his technique for secondary pyrolysis studies by matching his data to our previous results for the same conditions.

Concurrently, Ms. Yu will select and acquire organic standards to be used for calibrating the gravity-flow column chromatograph separation technique. These standard compounds will be chosen to represent a wide range of polarities and molecular weights, in order to span the range of compounds found in coal tar. Work will also begin on testing and refining the chromatographic procedure, using the standards.

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