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MAINTENANCE OF THE COAL SAMPLE BANK AND DATABASE

Quarterly Technical Progress Report

Contract Number DE-AC22-93PC93051

**The Pennsylvania State University
Coal and Organic Petrology Laboratories**

Reporting Period: 12/29/93 - 3/31/94

Report Date: 5/27/94

Contract Date: 9/28/93

Anticipated Completion Date: 9/28/98

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Principal Investigators: Alan Davis
David C. Glick

Program Manager: Gilbert V. McGurl

Contracting Officer's Representative: Udaya Rao

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Quarterly Technical Progress Report: 12/29/93 - 3/31/94

Objectives

This five year project is intended to ensure the availability of well-characterized, high-quality coal samples for public and private coal research. It continues support of the DOE Coal Sample Bank and Database at The Pennsylvania State University. Thirty coal samples will be collected, processed, packaged, and analyzed, and a resulting database will be maintained. These samples and data, as well as 26 samples collected under previous contracts, will be distributed to DOE contractors and others performing coal research.

Samples will be chosen to maintain a sample bank of 56 coals representing the major U.S. coal fields and a variety of coal ranks and compositions. In addition to standard analyses, liquefaction tests and organic geochemical analyses will be performed. The samples will be stored to minimize deterioration, and will be monitored annually by proximate, sulfur forms, and gaseous oxygen analysis to evaluate their condition. These samples will be used for additional research on the influence of changes in surface chemistry on surface properties, the influence of sample deterioration on liquefaction properties, and the mechanisms of coal oxidation.

Summary of Technical Progress

Task 1B. Storage and Inventory of Samples

All samples supported by the contract are stored in containers purged with argon before sealing; container locations are tracked by a computer inventory program. PSOC-series samples are stored in drums or buckets at the Coal Sample Bank building, or in cans in the Coal and Organic Petrology Laboratories. All DECS-series samples are stored under refrigeration in foil laminate bags.

During the quarter, splits of new sample DECS-23 were sealed, placed in storage, and added to the inventory. The inventory records for all samples were updated as samples were distributed.

Storage and inventory of sample containers is expected to continue routinely through the next quarter.

Task 1C. Monitoring of Sample Quality

One 300 g (2/3 lb) bag of each DECS sample will be analyzed annually to monitor sample condition. The first two-thirds of the first annual program was completed during the quarter. The new soft package sampling arm for the polarographic oxygen analyzer was used with success. This and other analyses show that in general, DECS samples in foil laminate bags continue to maintain their properties without deterioration.

The first annual quality monitoring program will be completed during the next quarter, and all results will be presented in the next Quarterly Technical Progress Report.

Task 1D. Collection and Processing of Replacement Samples

The first new sample of this contract, DECS-23 of the Pittsburgh seam, was collected on February 2, 1994 in Washington County, Pennsylvania. Approximately 220 kg (490 lbs) was collected as a whole-seam channel sample; associated blocks of coal were also collected. This sample will be used in particular for Task 1G. The sample was completely processed for storage in various sizes of foil laminate bags promptly after collection.

In order to plan sample collection trips, a list of the other 29 samples to be collected must be established. The contract contains a tentative list, but changes (such as inclusion of samples coordinated with HRI projects) have been suggested in past discussions with DOE. The list of samples to be collected has not been finalized or approved.

Task 1E. Basic Characterization of Coal Samples

Characterization of DECS-23 (Pittsburgh seam) was performed during the quarter. This sample was higher in sulfur (3.87 %) than DECS-12 (1.12 %), the other Pittsburgh seam sample.

Task 1F. Liquefaction Testing

Appropriate samples will be subjected to a standardized liquefaction test and subsequent product workup. The procedure developed for a standardized liquefaction test is detailed in Appendix A.

The new Pittsburgh seam sample (DECS-23) was tested during the quarter; results using tetralin are shown in Table 1. Because of problems with the 1-methylnaphthalene runs, both will be repeated.

Table 1. Conversion of DECS-23 (Pittsburgh seam) in standardized liquefaction test

			Conversion, %				
Sample	Replicate	Solvent	Total	Preasph.	Asph.	Oil	Gas
DECS-23	a	tetralin	60.91	28.14	6.79	7.75	18.23
DECS-23	b	tetralin	56.33	27.82	6.21	7.48	14.82
DECS-23	average	tetralin	58.62	27.98	6.50	7.62	16.53

This task includes a study to monitor liquefaction behavior in relation to sample storage. The study will begin with two samples collected in the first contract year.

Task 1G. Investigation of Changes in Surface Chemistry During Storage

The general objective of this task is to measure the changes in functional group concentration as a function of duration and type of storage method using reflectance-mode FT-i.r. and direct oxygen determination using electron optical techniques. Also, microscopic measurements of fluorescence alteration and intensity will be employed to determine the extent of surface alteration during coal storage.

A vitrinite concentrate was prepared from the fresh Pittsburgh seam sample (DECS-23). Five 2.0g subsamples of the concentrate were prepared and processed in a nitrogen-filled glovebox, where they were sealed in foil laminate bags before being placed in refrigerated storage. Proximate, ultimate and petrographic analyses have been completed, showing that the concentrate is 97 volume % vitrinite. Further base level fluorescence intensity and alteration measurements have been completed on both the whole-seam channel and vitrinite concentrate samples. Currently, the UMA 300A infrared microscope which will be used for functional group measurement is being evaluated using other samples. When the microscope is aligned and techniques are developed, the vitrinite concentrates will be evaluated.

Task 1H. Organic Geochemistry

Procedures for organic geochemical characterization were discussed and established internally during the quarter. Characterization of three to four existing samples will begin in the next quarter, and new samples will be characterized as they are collected. The existing samples to be characterized are:

DECS-2	hvCb	Illinois #6 seam	Illinois
DECS-8	subC	Smith-Roland ("Wyodak") seam	Wyoming
DECS-12	hvAb	Pittsburgh seam	Pennsylvania
DECS-17	hvAb	Blind Canyon seam	Utah

Task 1I. Distribution of Coal Samples to Users

During the period 12/29/93 - 3/31/94 a total of 12 samples (8 DOE Sample Bank samples and 4 other Penn State samples) of various sizes in 25 containers were distributed. Six of these samples were provided to DOE contractors. In addition, 24 bags of DECS-17 (for the DOE dispersed catalyst study) were distributed during the quarter. See Task 2C for a list of sample and data recipients. This task will continue in the same manner through the next quarter.

Task 2A. Programming

Programming required for the creation of the new data printout formats was a major activity during the quarter. This included extension of the capabilities of the program from incomplete two-page output to nearly complete five-page output. The user interface was written, several format decisions were made, and the coverage of the interactive Coal Database and the printouts were enhanced by the addition of several data fields from the old (tape-based) system. The majority of the work has been completed, and five-page or one-page printouts can be created with the new system. Further effort to replicate the coverage of the old format involves addition of some minor data fields, final

decisions on details of the format, and extensive checking against the previous program. This will be completed by May 15, when the old operating system will be discontinued. After that, further additions and improvements beyond the capabilities of the old system will be made.

Task 2B. Data Entry

Data for DECS-23 were added to the Coal Database during the quarter.

Task 2C. Distribution of Data to Users

During the quarter a total of 25 data printouts were distributed. In addition, 4 special data requests were fulfilled by database searches and output or creation of a data disk, resulting in distribution of limited information on 543 samples. Preliminary requests for Sample Bank and Database information and price quotations have also been filled. This task will continue in the same manner through the next quarter.

Organizations supplied with coal samples and/or data include:

ARCO Oil and Gas Company
 East Fairfield Coal Company
 Hokkaido University, Faculty of Engineering (Japan)
 Northeastern University
 Pennsylvania State University, Energy & Fuels Research Center
 Pennsylvania State University, Fuel Science Department (2)
 Pennsylvania State University, Geoscience Department (2)
 SRI International, Molecular Physics Department
 University of North Dakota, Energy and Environmental Research Center
 University of Utah, Chemistry Department (2)
 U.S. Department of Energy, Pittsburgh Energy Technology Center (2)
 Viking Systems
 West Virginia University, Chemical Engineering Department

The numbers in parentheses represent multiple requests which were separately processed.

References/ Publications

Penn State personnel collaborated on a paper which was presented at the American Chemical Society meeting in March: A Perspective on the Status of Coal Research from Shipments of Samples, 1994, Karl. S. Vorres, Carl W. Kruse, Koen A. Nater, David C. Glick and Alan Davis, Am. Chem. Soc., Fuel Chem. Prepr. 39:1, p. 1-6.

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APPENDIX A

Procedures for Standardized Liquefaction Test of DECS Samples including extraction and gas analysis

MATERIALS

Solvents (HPLC grade)

Tetrahydrofuran (THF)
Hexane
Toluene
1-methylnaphthalene 98%
1,2,3,4-tetrahydronaphthalene 99% (tetralin)

Equipment

Buchi RE111 Rotovapor
Omega XA-100 balance
Napco #5831 vacuum oven
sand bath reactor
stir plate

Bombs

4 tubing bomb reactors with 2000 psi pressure gauges and Swagelok fittings
approximately 24 ml capacity

Glassware and other supplies

(NOTE: all glassware is baked at 450°C prior to use; all other supplied
are rinsed with THF)

250 ml beakers
250 ml round bottom flasks
400 ml round bottom flasks
Soxhlet apparatus (for extractions)
Whatman glass microfibre filters (GF/C)
Whatman glass microfibre extraction thimbles (GF; 30x100mm)
boiling chips (cleaned with THF)
compressed nitrogen
gas-tight syringe
gas bulbs
metal spatula
magnetic stirrer
Petri dish

LIQUEFACTION

For each complete standardized liquefaction analysis, perform the following procedure for two tubing-bomb reactors using tetralin and two tubing-bomb reactors using 1-methylnaphthalene.

Ensure that baking of glassware and rinsing of other supplies has been performed.

All items which come in contact with sample or resulting products must be weighed to 0.0001 g before and after contact so that sample loss may be calculated.

Weigh out 5 grams of coal and 5 grams of tetralin (or 1-methylnaphthalene) and place both into the tubing bomb reactor.

Screw the end caps of the reactor on very tightly.

Fill and then purge the reactor with nitrogen up to 1000 psi (repeat 3 times).

Fill the reactor with hydrogen up to 1000 psi and then purge very slowly (over a period of 5 min.). Repeat 3 times. After the third fill, close the valve on the reactor, leaving it pressurized with hydrogen.

Submerge the reactor in water to check for leaks.

Place the reactor in a secure place where it is in a stable position. Observe the pressure reading on the gauge. If the pressure remains stable for 10 minutes you may assume no significant leaks exist.

Place the reactor into the sand bath which has been set at 350° C. The temperature of the sand bath will decrease rapidly after introducing the reactor. Wait until the temperature reaches 350°C and then begin timing the length of the run (30 minutes).

After 30 min remove the reactor from the sand bath and submerge it in water to cool the reactor.

At this point remember to keep the valve on the reactor closed and to store it in a secure place if it must be stored temporarily.

GAS ANALYSIS

Measuring the volume of gas

Attach a Swagelok purge valve with a 15 cm length of tubing onto the reactor, making sure that the valve on the reactor remains closed.

Onto the other end of the tubing, attach a flow-through gas bulb.

Onto the other end of the gas bulb attach a 1-meter length of tubing, so that the sequence is: reactor, Swagelok purge valve, tubing, gas bulb (for trapping gas), and a longer piece of tubing (1 meter).

Place the end of the longer piece of tubing into an inverted graduated cylinder filled with water. (For these reactions, gas production has been from 1-2 liters, so a 2 liter graduated cylinder is suggested.)

Make sure that the valves on the flow-through gas bulb are open.

Slowly open the valve on the reactor. Water should begin to evacuate from the inverted graduated cylinder as the gas displaces it.

When all the gas has left the reactor, close both valves on the flow-through gas bulb (trapping a sample of gas in the bulb).

Close the valve on the reactor.

From the inverted graduated cylinder, read the volume of gas that was in the reactor and record the data.

Take a gas-tight syringe and sample 1ml of the gas from the bulb. Inject the sample into the gas chromatograph.

The gas chromatograph is then run to analyze for CO₂ and C1, C2, C3 and C4 compounds.

After injection of the gaseous sample and the completion of the run, an external gaseous standard must be injected for a separate run (this will allow for the quantification of the sample injection).

Soxhlet extraction

Open the reactor.

Rinse the contents of the reactor into an extraction thimble (place the thimble in a 250 ml beaker) using no more than 200ml of toluene. The products will be adhered to the sides of the reactor and in the caps; scraping with the metal spatula will be necessary. **Be careful not to spill any sample; this is where the greatest chance for error lies.**

Take a 250ml round bottom flask, add boiling chips, and then attach to the Soxhlet apparatus.

Place the extraction thimble into the Soxhlet and then pour the contents of the beaker into the thimble. With more toluene, rinse the beaker into the thimble. Make sure that all of the sample is in the thimble and not lying in the bottom of the Soxhlet.

After all of the sample has been washed into the extraction thimble, add enough toluene to the round bottom flask to bring the total amount of toluene up to approximately 200ml (this includes the amount of toluene that is also in the Soxhlet).

Using tubing, connect the tank of compressed nitrogen to the condensing tower on the Soxhlet.

Turn on the nitrogen to the point where there is a light flow of gas going through the Soxhlet.

Turn on the water to the condensing tower.

Turn on the heating mantle and bring the toluene in the 250ml flask to a moderate boil.

At this point the toluene should start to cycle through the Soxhlet extractor.

Continue the extraction until the toluene in the Soxhlet has become colorless again. This takes approximately 48 h.

During this time it may be necessary to add more toluene to maintain a volume of 200ml.

After the extraction is complete, turn off the mantle and allow the solution to cool to room temperature.

Keeping the round bottom flask attached to the Soxhlet, tilt the assembly until the toluene in the Soxhlet pours into the 250ml round bottom flask.

After this is done, separate the 250ml round bottom flask from the Soxhlet and set the 250ml round bottom flask aside temporarily (these instructions resume below).

Take another 250ml round bottom flask, containing boiling chips, and fill it with approximately 200ml of THF.

Attach the 250ml round bottom flask to the Soxhlet.

Turn on the heating mantle and bring the THF to a moderate boil. The THF should start to cycle through the Soxhlet (remember, both the water and nitrogen should still be on).

This extraction should also take approximately 48 h. However, continue until the THF in the Soxhlet has become colorless again.

After the THF extraction is under way, return to the 250ml round bottom flask containing the toluene and toluene extractable material.

Transfer the contents of the 250ml round bottom flask into a 400ml round bottom flask. Be sure to rinse the 250ml round bottom flask (using toluene) into the 400ml round bottom flask at least 3 times.

Rotovaporate the 400ml round bottom flask, which will remove most of the toluene. (However, there will be some left, as well as some liquid product from the extraction).

After rotary evaporation, add approximately 400ml of hexane to the 400ml round bottom flask.

Add a magnetic stirrer to the 400ml round bottom flask.

Stir the contents of the 400ml round bottom flask for exactly 1 h.

After stirring, cover the 400ml round bottom flask and let it sit overnight.

The next day, filter the contents of the 400ml round bottom flask through the Whatman GF/C glass microfibre filters. Be sure to rinse the contents of the 400ml round bottom flask into the filter using hexane; rinse at least 3 times.

Transfer the filter paper, boiling chips, magnetic stirrer, and hexane- insoluble matter into a Petri dish (you may wish to rinse off the stirrer and remove it from the Petri dish before placing the dish in the vacuum drying oven).

Rotovaporate the hexane solubles (the solution not caught in the filter) to remove hexane. (This will remove most of the hexane; however, there will be some hexane as well as some liquid product from the extraction left in the round bottom flask).

Place both the Petri dish and the round bottom flask into the vacuum drying oven at 150° C for 2 h.

After drying, weigh the samples. The sample in the Petri dish is the asphaltene fraction. The sample in the round bottom flask is the oil fraction.

Return to the THF extraction:

Once the THF in the Soxhlet is colorless turn off the mantle and let cool to room temperature.

After cooling, turn off the nitrogen and the water.

Keeping the round bottom flask attached to the Soxhlet, tilt the assembly until the THF in the Soxhlet pours into the 250ml round bottom flask.

Wash all of the contents of the 250ml round bottom flask into a 400ml round bottom flask using THF.

Rinse the 250ml round bottom flask into the 400ml round bottom flask using THF at least 3 times.

Rotovaporate the 400ml round bottom flask (this will remove most of the THF; however, some THF and a liquid product from the extraction will be left).

Place the 400ml round bottom flask in the vacuum drying oven at 150° C for 2 h.

After drying, weigh the product in the 400ml round bottom flask. This is the preasphaltene fraction.

Remove the extraction thimble from the Soxhlet and place in the vacuum drying oven.

After drying, weigh the product in the thimble. This is the insoluble fraction.

Calculation of Product Distribution and Conversion

Apply the calculated sample weight losses from the before-contact and after-contact weighing of glassware and supplies to the appropriate steps in conversion calculation procedures.

insoluble residue weight = (wt. of thimble + wt. of sample remaining in thimble after all extractions are completed) - wt. of thimble (clean)

preasphaltenes weight = wt. of 250ml round bottom flask (containing boiling chips and dried extract) - (wt of 250ml round bottom flask (clean) + wt. of boiling chips (clean))

asphaltenes weight = wt. of Petri dish (containing boiling chips, dried extract, filter paper, and stirrer) - (wt. of petri dish (clean) + wt. of boiling chips (clean) + wt. of filter paper (clean) + wt. of stirrer (clean))

oil fraction weight = wt. of 500ml flat bottom flask (containing dried extract) - wt. of 500ml flat bottom flask (clean)

gas fraction (recovered using GC) weight = wt. of (CO_2 + C1 + C2 + C3 + C4)

weight of total recovered material = (wt. of insoluble residue + wt. of preasphaltenes + wt. of asphaltenes + wt. of oil fraction + wt. of gas fraction)

Conversion % for specific fraction = wt. of fraction x 100 % / wt. of original sample (before liquefaction)

Conversion % (total) = (wt. of preasphaltenes + wt. of asphaltenes + wt. of oil fraction + wt. of gas fraction) x 100 % / wt. of original sample (before liquefaction)

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7/29/94

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