Quarterly Technical Progress Report

Period Ending June 30, 1984

United States Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

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**QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD ENDING
JUNE 30, 1984**

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QUARTERLY TECHNICAL PROGRESS REPORT

April 1 - June 30, 1984

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EXECUTIVE SUMMARY

Sun W. Chun, Director

Considerable activity during this reporting period took place in the Department of Energy's Magnetohydrodynamics Program as the Component Development and Integration Facility in Butte, Montana, continued its site preparation for the TRW first-stage combustor installation. Most of the major construction has already been completed, and CDIF representatives are consulting with other contractors involved in this project to ensure an efficient and effective test program. At TRW, the design verification testing of the first-stage combustor development program was completed and the test results are very promising. During the next quarter, the combustor and its test stand will be delivered to the CDIF. Once testing is under way, TRW will build a second-stage combustor and another first-stage unit. These will be tested at TRW before becoming available for use in the MHD Program in 1985.

In the area of flue gas cleanup, our in-house research program is continuing its investigation into the causes of sorbent attrition in PETC's fluidized-bed copper oxide process for simultaneous SO_2/NO_x removal. Interwoven with these tests is a series of spray dryer/electrostatic precipitator tests that are being conducted with the cooperation of Wheelabrator-Frye, Inc. This test series was completed this quarter, and the data show that when using a Kentucky coal, Wheelabrator-Frye's electrostatic precipitator provides excellent particulate control efficiency while using a spray dryer for sulfur dioxide removal.

A unique project at Carnegie-Mellon University is looking at the concept of integrated environmental control for coal-fired power plants making use of precombustion, combustion, and postcombustion control, including systems for the simultaneous removal of more than one pollutant. The objective of this research is to develop a computer model and assessment for integrated environmental control systems that utilize conventional or advanced systems. A prototype model has already been assembled, as have performance and cost models for conventional components, and preliminary testing of the integrated model is under way. We expect that these models will be quite useful in future work involving advanced technologies, which by nature tend to have considerable technical, environmental, and economic uncertainties.

The Liquid Phase Methanol Project Development Unit in LaPorte, Texas, was restarted after a successful shakedown run was completed during the previous quarter. Despite some attrition, the catalyst remained highly active during the early stages of the run, maintaining a methanol production rate of 8 tons per day on a balanced feed gas. The mechanical performance of the PDU has been excellent, with no signs of erosion in the slurry pump or piping after almost 1,000 hours of operation. The results of a liquid-entrained run using a commercial catalyst will be reported in the next quarter.

The exploratory liquefaction testing in the continuous processing unit at Gulf's Merriam Research Laboratory was discontinued because of the planned shutdown of this research effort. The analyses of the final runs, which studied multi-stage processing of a Wyoming and a Texas coal, should be available shortly.

PETC has recently begun an in-house research project aimed at exploring the basic chemistry of liquefying coal in the presence of water under supercritical conditions. Through this effort, we hope to convert coal to a product suitable for upgrading to liquid fuels at the lowest possible cost. So far, we have found that a considerable fraction of the slurry oil used in coal liquefaction can be replaced with water before the conversion decreases significantly. In addition, we believe that by adding small quantities of ammonium molybdate catalyst to the process stream, the water might actually help to provide good catalyst distribution. Details of this project can be found in the section entitled "In-House Research and Development/AR&TD: Mechanistic Aspects of Liquefaction."

Lastly, in the Alternative Fuels Technology Program, the Gulf Research and Development Company has completed the preliminary testing phase of its erosion test loop. Their results indicate that when pumping a coal-water slurry fuel through a flow loop, the erosion rate increases as velocity increases, suggesting a well-defined relationship between these two parameters. More details of this project and the companion project at Combustion Engineering can be found in "Project Management and Support/Alternative Fuels Technology."

PROJECT MANAGEMENT AND SUPPORT

COAL LIQUEFACTION TECHNOLOGY PROJECTS

T.M. Torkos, Chief, Liquefaction Project Management Branch

The technical objectives of the Coal Liquefaction Technology R&D Programs are to seek advances and innovative improvements over the state-of-the-art processes for coal liquefaction that can utilize the entire U.S. coal resource base. Improvements in product selectivity and quality, net yield of liquid fuel products per ton of coal feed, and overall thermal efficiency are being sought, as are methods for integration of coal liquefaction into existing fuel-processing schemes to provide for near-term commercial applications. Improved plant operability and on-stream factors, as well as process and component improvements that reduce the capital and operating costs, are also being sought to provide increased economic viability. Mitigation of environmental and health impacts is a technical objective that will enhance the utility of coal liquefaction process technology. The following sections describe the current accomplishments of the R&D program.

Technical Support of Major System Acquisitions

The objective of this program is to provide technical support to the major coal liquefaction projects, which include the H-Coal pilot plant and SRC demonstration plants. This technical support is PETC-based technical support for the R&D support contracts.

H-Coal Pilot Plant Project

Ashland Synthetic Fuels, Inc.

The H-Coal Pilot Plant Final Report has been completed and distributed to DOE and the Project's Industrial Participants. Two reproducible copies were also sent to the National Technical Information Center (NTIC) for other distribution upon request. The report primarily covers the operating phase of the project and consists of ten volumes totaling approximately 3500 pages.

Since completing the final report, the processing of H-Coal Technical files for transfer to the PETC Liquefaction Technology Data Base (LTDB) had been primary task of Ashland Synthetic Fuels, Inc. (ASFI) for the past two months. A management plan was submitted by ASFI and approved by DOE. After gross separation of

nontechnical and other information mutually agreed to be excluded from information to be transferred to the LTDB, approximately 500 cubic feet of printed material remain to be processed. Processing includes removing proprietary data, both HRI and vendor, removing duplication, and copying all PETC material in both hard copy and microfiche. In addition to the printed material, plant drawings, copies of computer tapes of hourly average operating data, analytical analyses tapes, and computer programs will be transmitted to the LTDB.

The Management Plan schedules this task to be completed by AFSI in February 1985, with all deliverables to be in PETC's possession by March.

SRC Technology Assessment

Pittsburg and Midway Coal Mining Company

Pittsburg and Midway Coal Mining Company has completed drafts of all topical reports, including preheater studies, reactor dynamics, and technical uncertainties. These drafts should be submitted to DOE in the upcoming quarter. In addition, the final report is in progress. With this, all contract work should be completed in the final quarter of FY84.

Direct Liquefaction Technology Assessment

Oak Ridge National Laboratory

The final draft report for Integration of all subtasks in Task 1: "Technical Readiness of the Developing Plant Functions" has been received. The draft report for Task 2: "Plant Integration" has also been received. Thus all work on this project is essentially complete.

Advanced Process Development (Direct Liquefaction)

The overall objective of this activity is to develop, implement, and manage direct coal liquefaction industrial research and development (through PDU scale) projects for expanded use of coal as a petroleum substitute. Goals of this technological area are to (1) evaluate, develop,

and experimentally test, through integrated PDU scale, the feasibility of a two-stage approach for coal liquefaction to minimize hydrogen consumption while optimizing removal of contaminants to produce clean distillate fuels, (2) evaluate the use of alternative inexpensive materials or low material concentrations as liquefaction catalysts for reducing technology costs and increasing liquid product yields, and test selected material in continuous process units, (3) conduct basic and applied research studies to investigate potentially improved processes for direct coal liquefaction and to develop a better understanding of coal liquefaction systems, (4) experimentally evaluate the applicability of conventional petroleum-processing technology for refining of coal liquid into usable fuels; research, develop, and evaluate those refining and upgrading techniques necessary to prove the technology of coal liquids for their acceptability and compatibility with conventional fuels.

Wilsonville Process Development Unit

The initial attempt at integrated two-stage processing of a subbituminous coal began on March 31, 1984 (Run 246). Start-up was accomplished using solvent produced from the previous Illinois No. 6 coal run. Run 246 was also the initial attempt at operating a new slurry-drying system and testing of a new mode of ITSL processing in which only light deashed resid and thermal solvent were fed to the hydrotreater. The heavy deashed resid separated out in the Kerr-McGee Critical Solvent Deashing (CSD) Unit was recycled along with hydrotreated heavy solvent as first-stage slurry makeup solvent. The major objective of Run 246 was to define operability of the new slurry dryer and modified ITSL mode feeding Wyodak, Clovis Point Mine, subbituminous coal.

After some initial start-up problems were resolved, the new slurry dryer performed satisfactorily for the remainder of the run at coal feed rates of 250 to 300 lb/hr. Approximately three weeks' operation was required to allow the Illinois No. 6 start-up solvent to be diluted out of the ITSL system. In late April, operations were temporarily interrupted to determine if an observed temperature maldistribution in the dissolver was due to solids buildup. The dissolver was inspected and found to be normal, with no signs of significant buildup. The dissolver temperature distribution problem was thought to be responsible, at least in part, to an observed gradual loss in coal conversion and consequently to a reduction in CSD Unit separation performance. In a concentrated effort

to reverse deterioration run performance, several changes in operating procedures and run conditions were implemented during the latter part of May. Dissolver temperature control, previously based on dissolver outlet temperature, was rebased on average dissolver temperature, which was then maintained at 825°F. Coal feed rate was reduced from 300 to 250 lb/hr. Hydrotreater reactor temperature was increased to 630°F from a previously reduced temperature of 610°F. The net effect of the above changes was to increase coal conversion from 87% to an acceptable 92%, and CSD Unit separation performance was also improved substantially.

On June 13, 1984, PDU operation was changed from the Doubly Integrated Two-Stage Liquefaction mode, with only light deashed resid feed to the hydrotreater, to the standard ITSL mode in which both light and heavy resids are fed to the hydrotreater. An usually high pressure drop first observed on June 6, 1984, continued to increase during ITSL mode operation; and on July 1, 1984, when the pressure drop had reached 700 psi, the PDU was voluntarily shut down to determine the cause of the problem.

Thermal Liquefaction Unit Operations

Throughout Run 246, a disposable iron oxide catalyst effective in bench-scale testing was added at a rate equivalent to 2 wt% on coal feed. Additional sulfur was also added in the form of dimethyl disulfide to ensure conversion of the iron to the sulfide state.

The abnormal axial dissolver temperature profile experienced essentially throughout Run 246 has been attributed primarily to a secondary exotherm occurring in the upper half of the dissolver. Maintaining dissolver outlet temperature at 825°F provided an average dissolver temperature of about 805°F. Controlling average dissolver temperature at 825°F increased outlet temperature to 840°F to 845°F.

Kerr-McGee CSD Unit

Several incidences of ash carry-over and poor separation performance were experienced during most of the first two months of operation. Several adjustments in deashing-solvent composition, operating conditions, and instrument calibration were required to achieve good stable performance. Energy rejections equivalent to the best obtained in previous operations with Illinois No. 6 coal were achieved.

H-Oil Hydrotreater Unit

The hydrotreater was started up with a fresh batch of presulfided Shell 324M catalyst and operated throughout the run in the batch mode (no catalyst addition/withdrawal except for small samples taken for future analysis). The catalyst was particularly effective for conversion and hydrogenation of the light deashed resid/heavy thermal solvent feed. Reactor temperatures of 610°F to 650°F were used, with an average of about 630°F for the run. Light resid conversions of 20% to 25% were typically obtained at 630°F.

Two-Stage Liquefaction

New Technology Concept for Two-Stage Liquefaction of Coal — Hydrocarbon Research, Inc.

The major activity during this quarter was the operation of the continuous bench unit. Two scoping runs were completed and a third run was started during this reporting period. Efforts were primarily centered around optimizing the operating temperature, investigating new catalysts and recycle modes, and operating at a higher system pressure (2500 psig).

Bench Run 227-16 was started in late March and was intended to duplicate Bench Run 227-15, which was the thermal/catalytic base-line run. Unfortunately, the run was terminated after only 13 days of operation owing to a high pressure drop in the first reactor, apparently caused by a buildup of carbonaceous agglomerates. Distillate yields at comparable conditions were only marginally higher during this run than in the thermal base-line run.

Bench Run 227-17 was started on April 14, and three major changes were incorporated into the run.

- a. The system pressure was raised to 2500 psig. All previous bench runs had been made at 2000 psig.
- b. Amocat 1C catalyst (Ni/Mo) was used in the first stage, and Amocat 1A (Co/Mo) was used in the second stage.
- c. Recycle of vacuum still bottoms (solids and residuum) was accomplished during two of the eight operating periods.

A wide range of temperatures, 560°F to 750°F, were investigated, and the run yielded the best results obtained to date. Highlights are summarized below:

- a. C₄-954°F distillate yields in the 59% to 65% range, based on maf coal, were obtained for all but one operating condition.
- b. Consistently low (5% to 7%) C₁-C₃ gas makes were attained at all operating conditions.
- c. Sulfur and nitrogen removals were the highest attained to date.
- d. Filterability of topped separator bottoms was good, indicating a low viscosity resid.
- e. Hydrogen efficiency (distillate yield/H₂ consumption) was high (at approximately 12).
- f. An apparent low rate of catalyst deactivation was calculated.

All of the above were accomplished at a comparatively low operating severity [<2.5 , Standard Time Temperature Unit (STTU)].

Bench Run 227-18, which was started in mid-June, is to be the final scoping run before the Illinois No. 6 coal demonstration run. A sampling device has been installed between the two reactors so that first-stage effluent can be sampled and tested in an effort to determine the impact of the first stage on the overall process. This run is also intended to pinpoint the best operating temperature and recycle scheme. Bench Run 227-18 is operating at the same pressure and uses the same catalysts as Bench Run 227-17.

When work on Illinois No. 6 coal is completed in July, work on the second coal (Clovis Point, Wyodak Coal) will begin. If time and money permit, a less expensive coal from a Pittsburgh Seam will also be tested.

Also, when investigation of Illinois No. 6 coal is completed, the following engineering evaluations will be conducted:

- a. Improve quantitative understanding of the new two-stage technology vs. alternative coal liquefaction approaches.
- b. Develop preferred process flow schemes and assess feasibility of the integrated process step.
- c. Evaluate the process economics to provide guidance to the ongoing research program and establish an overall plant configuration.

The engineering portion of the program has been delayed until reasonable operating parameters and results have been established for Illinois No. 6 coal.

In recent months, the microautoclave (MA) has not been operated as a scoping tool but rather

only in a support effort to the bench unit. In the past, MA results when operating in a two-stage mode have not been comparative to bench-run results. Consequently, its use as a scoping tool in the two-stage mode has been questionable. The MA can be a quick and less costly scoping tool if confidence in its use can be gained. In a final attempt to obtain a MA/BR correlation, the following steps were taken: (1) a second sand bath was installed; (2) catalyst preparation (presulfiding) was changed; (3) reactor loadings — solvent/catalyst/coal — were reevaluated; and (4) analytical procedures were revised.

A test program to evaluate the effect of these changes is presently under way.

Integrated Two-Stage Liquefaction Research

Lummus Integrated Two-Stage Coal Liquefaction

The goal of this technological area is to evaluate, develop, and experimentally test, through PDU scale, the feasibility of a two-stage approach for coal liquefaction to minimize hydrogen consumption while optimizing removal of contaminants to produce clean distillate fuels.

Task 4, the Deasher Study, was completed. Task 3 was also completed with a draft final report of the conceptual commercial Short Contact Time (SCT) design. Subtask 2.2.1.1 was started as the first part of the enhanced Task 2 program. A model of LC-Fining reactions and kinetics was formulated; activation energies for 650°F+ and 850°F+ conversion were calculated from Task 2 results. The low pressure SCT operation showed no effect on conversion or yields. The performance of extract made at low pressure (500 and 1000 psig) in the deasher and LC-Finer was indistinguishable from extracts made at high pressure.

Subtask 1.2 (Modified) -

SCT Reactor Modifications in the ITSL PDU

Material balance calculations have been completed for the last ITSL PDU runs. The SCT operation at 500 and 1000 psig had no effect on any of the unit operations. The 500 psig runs, however, were at the lowest severity SCT conditions used to date. The C₁-C₃ gas yields were predicted by our severity factor and were in the range of 1.0% of coal. Light distillate yield was also low; the few data points obtained indicate that low-pressure SCT operation will maximize the yield of extract and heavy distillate.

The 3LCF unit processed the extract made at low pressure with no noticeable effect on catalyst

performance. Although most of the catalyst age had been completed with Wyodak extract, catalyst activity for conversion and denitrogenation of Illinois extract was the same for Run 3LCF9 at the same catalyst ages. This shows that catalyst activity is feed-dependent and is independent of prior history.

Task 2 - LC-Fining PDU Support

Activation energies of conversion were calculated for Wyodak and Illinois No. 6 extracts. The major difference between the two feeds is the much higher activation energy of 650°F+ material from Wyodak. This indicates that the 650°F to 850°F product from Wyodak is more susceptible to thermal cracking, and a relatively small increase in LC-Fining temperature will result in a -650°F product.

Subtask 2.2.1.1 was started and is scheduled for completion in July. In this run, the LC-Finer will be operating at four different conditions to determine the effect on conversion of heptane solubles. For most conditions, space velocity will be 1.5, corresponding to the first reactor of the 3LCF unit. The products will be vacuum-flashed, with the overhead subsequently being the feed for the next subtask. The bottoms will be characterized as SCT solvent. Feed for this subtask is extract made at the end of Subtask 1.2.

Task 4 - Deasher Study

The purpose of this Task is to study deashing parameters so that the size and cost of the deasher may be reduced. One investigation carried out was to increase overflow velocity. This results in more ash carry-over in the overflow extract, but to some extent, the LC-Finer can tolerate this, as has been demonstrated in Tasks 1 and 2. The Task is essentially complete, and the data will be analyzed and reported upon in the next quarter.

Cleanup and Shutdown

The ITSL PDU, New Brunswick Facility, was shut down after all process equipment had been flushed. The PDU is now in standby condition. Most liquids and semiliquids have been disposed of. Solids (coals and extracts) will be disposed of in July and August. There are still many analytical samples and small containers of materials that must be blended before they can be sent out.

Task 2 - Enhanced Program

A major modification was made to the contract. A subtask was added to the Task 2 program for

concentration on second-stage conditions needed to maintain previously demonstrated short-contact-time solvent quality. The contract term was also extended to March 31, 1985, an additional nine months beyond the scheduled contract expiration date.

Kerr-McGee Advanced Direct Coal Liquefaction

Three runs were completed on the integrated bench-scale unit this quarter feeding Illinois No. 6 bituminous and Clovis Point subbituminous coals. A modified Integrated Two-Stage Liquefaction (ITSL) mode of operation in which only light deashed resid and thermal solvent are fed to the hydrotreater was used for all three runs. The heavy deashed resid separated out in the Critical Solvent Deashing (CSD) Unit is recycled to the Thermal Liquefaction Unit (TLU) as part of the coal slurry solvent. The Illinois coal operations were conducted to determine the effectiveness of the modified ITSL mode to process bituminous coal and to determine the effectiveness of a porous iron oxide catalyst added to the TLU at the rate of 2 wt% of mf coal. The effect of adding additional sulfur (1 mole sulfide/mole of added iron oxide) to the TLU system was also examined. The modified ITSL mode was very effective for processing the Illinois Coal. The most significant improvement as a result of adding the iron oxide was a decrease in the preasphaltene content of the vacuum bottoms from 24% down to 16% on a soluble-coal basis. Coal conversion increased from 93.0% to 93.7%, and coal rejection to ash concentrate was reduced from 21% to 18% mf coal. The effect of additionally adding sulfur (as dimethyl disulfide) was to further lower the preasphaltene content in the vacuum bottoms to 13 wt%.

Operations with Clovis Point subbituminous coal were conducted to test an experimental CSD Unit secondary extractor on high-solubility vacuum bottoms typically produced from this coal.

Rotating Disc Contactor Deashing — Foster Wheeler Energy Research Corporation

During this program, the Foster Wheeler Rotating Disc Contactor (RDC) will be evaluated for the deashing of coal-derived liquids. The RDC has been used extensively for solvent deasphalting of petroleum residues. Its use for deashing is based on the concept that deasphalting is a solvent extraction operation in which lower molecular weight and less aromatic fractions are

preferentially extracted from a hydrocarbon mixture. The heavier and more aromatic fractions, along with any insoluble mineral matter and most of the soluble metal-organic compounds, are left behind.

Initially, batch tests will be used to screen a variety of conditions. Following the completion of the batch-deashing tests, a series of runs will be made in a continuous countercurrent RDC deasphalting unit. While lacking the degree of fractionation possible in continuous countercurrent operation, the batch runs can be expected to produce approximate yield and quality relationships. They will also produce a wide range of general information on solvents to be tried and approximate operating conditions for the subsequent RDC runs.

A kickoff meeting was held at Foster Wheeler Development Corporation. It was attended by the DOE/PETC Technical Project Manager, the HQ Program Manager, and the appropriate contractor personnel.

Three main product quality targets were identified:

- 0.01 wt% ash in 850°F + RDC overheads
- 80 wt% or better recovery of the 850°F + ash-free feed in RDC overhead (74.8% or better on the feed)
- 50 wt% or better solids [quinoline insolubles (QI)] in the RDC bottoms (79.6% or better on the feed)

The Work Plan Schedule of Inspections was revised to add new inspections that will aid in evaluating performance, and to eliminate others because they are redundant or not applicable to the feedstock.

Eighteen drums of fresh vacuum bottoms material from Wilsonville were received and will be used as the deasher feedstock for this program. Extensive characterization of this feedstock has also been completed.

Analyses of the feedstock are summarized in Table 1. The feed contains 10.2 wt% solids (QI) and 6.5 wt% ash.

The batch test run phase of this project is now nearly complete; 23 out of the 30 projected runs have been done. Some preliminary conclusions can now be drawn. Deashed oil products of 76.7 wt% to 82.5 wt% (or 82.0% to 88.2% on ash-free feed) with an ash content below 100 ppm were obtained in five different runs.

Table 1.
Inspection of Deasher Feedstock

Specific Gravity at 60/60°F	1.297
Absolute Viscosity at 350°F, cP	45,560
Absolute Viscosity at 450°F, cP	453.0
Conradson Carbon Residue, wt%	56.6
Quinoline Insolubles (solids), wt%	10.2
Insoluble Organic Matter, wt% (by difference of quinoline insolubles and ash)	3.7
Softening Point, °F	320
Solvent Fractionation of RDC Feed, wt%	
Oil	52.6
Asphaltenes	20.9
Preasphaltenes	7.5
Tetrahydrofuran Insolubles	19.0
Distillation, °F*	
IBP	770
2 vol%	860
5 vol%	920
8† vol%	950
Ultimate Analysis, wt%	
Carbon	83.14
Hydrogen	5.71
Nitrogen	1.30
Sulfur	1.00
Oxygen	2.47
Ash	6.5
Metals, ppm (wt)	
Titanium	434
Nickel	8
Calcium	2,150
Vanadium	25
Iron	9,376

*Temperatures are reported at atmospheric pressure.

†Distillation ended when thermal cracking occurred at a still temperature of 650°F.

**Preliminary Runs with Toluene as Solvent
(Runs 1, 2, and 3)**

The three initial runs were made with toluene at a nominal 8:1 solvent-to- extract ratio to explore

the effect of temperature in the region somewhat below the critical temperature. In Run 2, an unsuccessful attempt was made to improve the yield by washing the asphalt. This was discontinued in subsequent runs. Run 3 at 540°F produced the de-

sired deashed-oil yield of 80% on the ash-free basis. The ash content was 770 ppm, as compared with the desired 100 ppm.

Dioxane as Solvent (Run 4)

Run 4 was made with dioxane as the solvent at 8:1 ratio and at 570°F, with the thought that a higher solvent power solvent at a higher temperature would afford better settling and would permit better stripping of the residue by decreasing its viscosity for better mass transfer. This produced about 7% higher yield and appreciably lower ash content (320 vs. 700 ppm) deashed oil than in Run 3, as expected. Because the deashed oil, however, showed 4.59% oxygen content, as compared with about 2.84% on a comparable run with toluene, the dioxane was deemed too reactive for further consideration.

Effect of Solvent Ratio (Runs 5, 6, 7, and 18)

To explore the effect of solvent ratio, Runs 5, 6, 7, and 18 were made with toluene at 540°F and ratios ranging from 4:1 to 12:1. Also, Run 7 at 8:1 (check on Run 3) was allowed to settle for twice the normal time after the usual mixing. The ash contents of the deashed oils from Runs 3 and 7 were in close agreement, indicating that the normal settling time is sufficient.

All of these runs produced nearly the same yields, which fell within the desired range. Inexplicably, 4:1 ratio produced about the same ash content deashed oil as 8:1. The runs at 8:1, 10:1, and 12:1, however, point toward a consistent inverse relationship between deashed overhead (DAO) ash content and solvent ratio. The data indicate that high solvent ratios are a critical factor in obtaining low ash content product. It should be noted that Run 5 at 12:1 toluene at 540°F produced the desired DAO yield and an ash content of 60 ppm, well below the desired 100 ppm. It should be noted that 12:1 ratio is by no means out of line with our experience for best operation at such high yields in petroleum residue deasphalting operations.

Heptane as Solvent (Run 8)

Run 8 was made with normal heptane at 8:1 and at 500°F, to extend the yield-quality relationship of Runs 1, 3, and 7 into the low-yield range.

Toluene-THF Blend Solvent (Run 9)

To determine whether operation with a stronger solvent at a higher temperature would produce the desired ash content DAO at the desired yield

without raising the solvent to extract ratio above 8:1, Run 9 was made with 80% toluene - 20% THF blend and at 570°F. Some improvement was noted but not enough to justify further consideration of this operation.

Xylene as Solvent (Runs 10, 11, and 12)

To further study the effect of operating at higher temperatures, Runs 10, 11, and 12 were made using xylene at 8:1 and 12:1 at 590°F, and 8:1 at 615°F. It is notable that 8:1 and 12:1 runs showed an ash content vs. ratio relationship parallel to that of the corresponding toluene runs. Ash contents were higher than for the corresponding toluene runs, in line with the higher DAO yield (81% to 82% vs. 75% to 77% for toluene). Had these runs been made at a slightly higher temperature, the results probably would have coincided. Run 12 at 8:1 ratio and 615°F, gave a DAO ash content essentially the same as the corresponding toluene runs, although at a slightly lower yield. As this high temperature operation appeared to offer no significant advantage over operation in the 550°F to 570°F range, and because temperatures above 600°F are beyond the operable range of the RDC, no further consideration was given to this type of operation.

Effect of Temperature on Deashing (Runs 13 through 17 and 19 through 23)

To further explore the effect of deashing temperature at 12:1 solvent ratio, the above runs were made with toluene, a blend of toluene and xylene, and a blend of toluene and heptane. The results indicate that for toluene, an optimum yield of about 80 wt% is obtained in the 550°F to 570°F range. This is very much in line with our experience in petroleum residue deasphalting. If the extraction temperature is reduced beyond a certain point, the normal trend toward higher yields is reversed because the residue phase (solvent-lean or raffinate phase) becomes too viscous for mass transfer, and therefore equilibrium cannot be obtained and extraction is incomplete. Increased surface tension and other factors, such as lower settling rates, also may enter in at the lower temperatures. For this reason the normal yield vs. quality curve and the yield vs. extraction deashing temperature reverse themselves, respectively, as does extraction (deashing) temperature vs. quality. As the optimum yield vs. quality range appears to be so narrow and offers such low ash content, runs in this range are being checked.

The RDC continuous deasphalting unit was revamped for high-temperature operating, and

debugging tests were carried out using Mayan vacuum residue in June. Runs with coal liquid feed will begin in July.

As of the moment, a deashing operation using toluene at approximately 12:1 solvent ratio in the range of 540°F to 570°F appears to be the way to produce 80% of deashed oil of less than 100 ppm ash, and a residue of at least 50% quinoline insoluble on an ash-free basis. These conditions produce optimum yield and ash content at the same time.

It is expected that continuous countercurrent operation will produce similar yield and ash content at a somewhat lower solvent ratio for similar temperatures.

In subsequent batch runs, an attempt will be made to operate at the same ratio and temperatures as in previous runs but with a solvent blend consisting of xylene and a heavy, highly paraffinic solvent. The purpose of this is to try to develop a satisfactory operation at pressures considerably lower than those needed for toluene.

Advanced Research for the Characterization of Hydrogen Donor Solvents in Two-Stage Liquefaction — Cities Service

The purpose of this research program is to develop an improved method for producing a highly effective solvent for the Integrated Two-Stage Liquefaction process and to study the characteristics of the solvent at a variety of process conditions.

Microautoclave studies pertaining to the production of an improved extraction solvent were continued in this quarter. Four solvents were characterized thoroughly, both by analytical techniques and by running solvent-only runs to determine the extent of reactions attributable to the solvent in the absence of coal under Short Contact Time (SCT) conditions. The four solvents cover a range of hydrogen content from about 6 wt% to 9 wt%. For each of the four solvents, little to no conversion of liquid to gas or solid products occurred, even at the most severe operating conditions, namely 900°F, 200 psig H₂ pressure, and 8 minutes residence time. Likewise, there was no detectable hydrogen consumption. Preliminary findings for the solvent containing approximately 7.5 wt% hydrogen indicate that a level of preasphaltenes in the solvent tends to increase by a small amount, i.e., 1% to 2%. The level of insoluble material in the solvent remained unchanged on reaction at SCT conditions. At high SCT severi-

ty, namely 850°F, 2500 psig H₂ pressure, and 10 minutes, the oil content increased slightly at the expense of preasphaltenes and asphaltenes. Elemental composition of the solvent remained unchanged.

Based on the findings discussed above, for solvents being studied in this program, no major changes in the solvent occur at SCT conditions. An abbreviated set of solvent-only runs was made under a nitrogen atmosphere. Again, no significant conversion of solvent to gas or solid products was observed. Data on compositional changes under nitrogen are not yet available. Because all data received to date indicate no major changes in the solvent at SCT conditions, the net yields previously reported for Illinois No. 6 coal in these solvents show valid trends, unaffected by changes in the solvent. Data and methods are now developed, however, to adjust for the small solvent changes in coal SCT runs, and this information will be incorporated into the data analysis for the entire program.

A series of SCT runs using Illinois No. 6 coal and each of the four solvents, under both hydrogen and nitrogen, was performed. Based on preliminary results for solvents containing 7.4 wt% and 8.6 wt% hydrogen, the following observations were made regarding the use of nitrogen vs. hydrogen: overall coal conversion is suppressed by about 0 wt% to 20 wt% under nitrogen. The greatest degree of suppression occurs at high levels of severity, where hydrogen demand is greatest.

The greatest liquefaction conversions were realized with solvents containing approximately 7.5 wt% hydrogen. The solvent containing 6 wt% hydrogen had the lowest conversion. Generally, coal conversions were relatively low at low-severity conditions, i.e., 700°F and 2 minutes, and increased with rising severity. Conversion improved with an increase in pressure from 500 to 2500 psig, especially with the less-active solvents, 6 wt% and 9 wt% hydrogen, respectively.

Several hydrotreating and hydrocracking catalyst samples have been received. Modified Shell 324M Ni/Mo catalyst was selected as the base-case catalyst, because of its known good performance in the LC-Fining stage of Integrated Two-Stage Liquefaction. Solvent-only runs using this catalyst and a 7.7 wt% hydrogen solvent were made at a variety of operating conditions as a basis for selecting run conditions for upcoming hydrotreating and hydrocracking runs.

Disposable Catalysts

Research on Coal Liquefaction — Gulf Research and Development Company

Exploratory coal liquefaction testing in the continuous processing unit at the Merriam Research Laboratory was discontinued at the end of April due to the planned shutdown of the overall research effort at Merriam. Final runs on the unit were made to study the multistage processing of a Wyoming subbituminous coal and a Texas lignite. The final analytical work on these runs, and the data analyses have not yet been completed.

The SRC worker epidemiology development task was continued with performance of quality checks of the SRC data files to ensure that all data were accurate and meaningful. Industrial hygiene data tapes from SRC operations were evaluated to establish data files containing specific process-related exposure data. Relevant information on all 569 SRC workers were provided to the Social Security Administration to achieve a data search for vital status follow-up. Computer programming to produce easily reportable information on the employee and industrial hygiene surveys has been started in advance of issuing a detailed project status report.

Enhanced Catalysis by Solvent Improvement — Air Products and Chemicals, Inc.

The objectives of this work are the preparation of modified solvents and the evaluation of coal liquefaction in these solvents; the development of data that demonstrate the catalytic activity of various materials for improving coal liquefaction in modified solvents; the determination of the effect of coal preparation on liquefaction yield under catalyzed coal liquefaction with and without solvent modification; and the evaluation of alternative techniques for preparing large batches of modified solvents for use in a batch autoclave from which the process solvent will be recovered and characterized for the level of contaminants.

Work continued with resid recycle in the presence of a molybdenum catalyst to determine the sensitivity of oil production to the amount of resid recycled. Oil production decreased from 71 wt% to 60 wt% when the resid concentration in the recycle solvent decreased from 33 wt% to 21 wt%. Overall coal conversion and gas production changed marginally when the SRC concentration in the recycle solvent was changed.

An Illinois No. 6 coal sample was prepared by fractionating a 2-inch by 10-mesh portion of the coal sample into eight specific gravity fractions

that were analyzed for ash content. The variation in ash was from 3 wt% to 75 wt%. The fractions containing less than 20 wt% ash were submitted for detailed analyses, which are not yet available. Samples from the fractions will be liquefied in a tubing-bomb reactor with and without catalyst to ascertain the effect of indigenous coal minerals upon liquefaction.

A large batch of modified solvent was prepared for use in a semicontinuous unit (batch autoclave) recently designed and fabricated. The unit will be used for testing the effect of solvent modification on catalytic and noncatalytic coal liquefaction at a scale of operation larger than that used in earlier tasks performed with tubing bombs.

Improved Dispersion Techniques for Slurry Phase Catalysis — Auburn University

The objectives of this work are (1) the identification of metal sulfides and supports for fabricating novel microsupported catalyst systems; (2) the preparation of types of highly dispersed microsupported catalyst systems using different preparative procedures; (3) characterization of the catalyst systems for porosity, particle size, total surface area, active component surface area, and dispersion of the active phase; (4) evaluation of kinetics, selectivity, and activity maintenance of the above materials; (5) recharacterization of spent catalysts to determine primary stability considerations and deactivation mechanisms; and (6) selection of the most promising materials and determination of the function of the materials using model compound studies to redesign, tailor, and optimize their performance for coal liquefaction.

Catalyst Preparation

Supported metal catalysts containing Ru, Fe, Mo, and W have been prepared by treatment and subsequent decomposition of appropriate dodeca- and hexa-carbonyls onto Saffils (Imperial Chemical Industries), silica gels, and other supports. These supports permit stable and high surface area materials to be prepared that possess minimal porosity. These catalysts have thus provided a means for assessing the inherent effects of the catalytic agents in the absence of intraparticle heat and mass transfer and/or deactivation by either pore mouth plugging or pore mouth narrowing.

Catalyst Characterization

Activity tests have been performed in batch reactor studies (700K to 750K, 8720 kPa) to determine the conversion of coal to pentane-soluble

oils and also in a continuous differential reactor (623K, 101 kPa) using appropriate model compounds.

Model reactions reveal that changes in the crystallite size below ca. 15 nm provide a means for increasing the inherent hydrodesulfurization-to-hydrogenation activity ratio by an order of magnitude.

Batch reactor studies at a low-catalyst-loading range (0 to 0.3 m² of active surface per g maf coal) and at a high loading (~70 m²/g maf coal) demonstrate highly different responses in oil yield to variations in active-surface area. At low loadings, beyond the increases in oil yield that occurred with initial catalyst addition (from 18% to 30%), no further increases in oil yield greater than ca. 30% occurred even with as much as 10 times more active surface area added. At a high loading (70 m²/g maf coal) of NiMo/Al₂O₃ pellets (225 m²/g), grinding the pellets to a powder to decrease the diffusional path length resulted in about a 16% increase in oil yield. These differences in responses at low and high loadings are temporarily attributed to either (1) a changing reactant composition beyond 30% conversion or (2) a product inhibited reactant sequence.

Spent Catalyst Evaluation

Reactor-modeling studies have also been done to evaluate the relative importance of catalyst deactivation and regeneration rates on overall activity. Order of magnitude activity improvements are shown to be possible with parallel catalyst regeneration.

Catalyst Improvement

Studies are under way to measure the responses in oil yield to variations in catalyst porosity, degree of catalyst dispersion on the substrate surface, and substrate design. Changes in the substrate design intended to decrease diffusional pathlength are hoped to be done via creating ~10-micron-size channels in 1/8-inch catalyst pellets, dividing the macropellet structure into domains of about 100 microns in size. Parallel studies are ongoing to evaluate the hydrogenation activity response of specific coal product fractions having different molecular sizes to changes in catalyst pellet sizes ranging from ground powder to 1/8-inch pellets.

Advanced Preparation for Direct Coal Liquefaction — Battelle Columbus

Advanced preparation evaluations are being conducted on both the Illinois No. 6 and the

Wyodak project coals in advance of the comparative evaluation of their coal liquefaction behavior.

Experimental work with the Illinois No. 6 coal is nearly completed. Chlorine removal tests on this coal show that the amount of removal using pressurized water treatment is increased with increasing time and temperature. The bulk of the removal is achieved in the initial 15 minutes. The buildup of chlorine in the leaching water does, however, decrease the amount of chlorine removed from the coal. Initial investigations have shown that it is feasible to incorporate disposable catalysts into the coal during this chlorine removal operation. Additional work will be conducted to further evaluate the potential usefulness of this technique.

Mineral matter separations on the Illinois No. 6 coal using specific gravity (float-sink) techniques show that the ash in this coal is finely disseminated. Treatment of this coal in oil agglomeration indicates that greater than 5% by weight of oil and a mixing time of 2 minutes are required to form agglomerates. Light oil forms agglomerates at lower oil-to-coal ratios than those achievable with heavy oil. Increasing the oil-to-coal ratio also increases the amount of water rejection during agglomeration. In combining the chlorine removal and the oil agglomeration steps, it was determined that the oil agglomeration operation was not affected by the chlorine removal step if the temperature of the chlorine removal step was kept below 200°C. Pyrite retention in the coal during oil agglomeration was good.

A hot solvent drying apparatus has been constructed to enable this operation to be conducted in an inert atmosphere at temperature while permitting visual observation of foaming behavior and possible viscosity effects. Procedures for conduct of this operation in a safe and satisfactory manner are being developed.

For the coal liquefaction tests, standard reaction test conditions of 427°C, five-minute reaction time, 2:1 solvent:coal ratio, and 1000 psig initial hydrogen pressure have been identified as resulting in good conversions in both the Illinois No. 6 and the Wyodak coals. An existing microautoclave reactor system for conduct of coal liquefaction tests is being modified to permit the simultaneous liquefaction testing of up to five coal samples. This modification will ensure a better consistency of the sample time-temperature profiles during comparative liquefaction tests of alternatively treated samples.

Table 2.
Analyses of Illinois No. 6 Coal
(PSOC 1188: Burning Star No. 4 Mine)

Proximate Analysis	(as-received basis)
Moisture	8.79
Ash	15.55
Volatile Matter	24.77
Fixed Carbon	50.89

Ultimate Analysis	(daf basis)
C	77.54
H	5.41
O (diff)	10.17
N	1.58
S (tot)	5.29

Maceral Composition
(dmmf volume %)

	Wyodak, Clovis Point Mine (PSOC 1401)	Illinois No. 6, B.S. No. 4 Mine (PSOC 1188)
Vitrinite	84.8	88.0
Fusinite	2.8	2.1
Semi-Fusinite	6.7	7.6
Macrinite	0.9	0.7
Micrinite	3.0	0.9
Exinite	1.8	0.7

Mean Max. Vitrinite reflectance	0.42	not available

The cumulative effects of the advanced pretreatment steps on coal liquefaction were examined using treated coals that were dried in a vacuum oven at room temperature under nitrogen to eliminate any effects due to moisture-level differences. Pretreatments involving chlorine removal followed by drying, as well as oil agglomeration followed by drying, had beneficial effects on liquefaction yields. Solvent drying also produced a positive effect upon liquefaction yield. However, initial results from coal treated in sequence through all pretreatment steps showed a slightly decreased conversion compared to the processing of untreated dry coal.

***Effect of Coal Constituents and Their Removal
on Two-Stage Liquefaction —
Pennsylvania State University***

Samples of recycle solvent have now been obtained from the Lummus Integrated Two-Stage

Liquefaction unit. These solvents were obtained from runs with both Illinois No. 6 and Wyodak coals. Both recycle solvents have been separated into -850°F distillate and + 850°F fractions.

Since efforts to obtain unground samples of the two coals that have been tested at Lummus and Wilsonville have proven less successful, the Pennsylvania State University Coal Sample Bank was searched to determine if samples were available that would closely match the sources of the original coals. The coals tested in the Lummus and Wilsonville units were Illinois No. 6, Burning Star No. 2 Mine; and Wyodak, Clovis Point Mine, Upper Seam. The following samples have been located in the Sample Bank in sufficient quantities for initial pretreatment and liquefaction experiments: Illinois No. 6, Burning Star No. 4 Mine, PSU number PSOC 1188; and Wyodak, Clovis Point Mine, Upper Seam, PSU number PSOC 1401. Available analyses are summarized in Table 2.

The literature surveyed thus far is being summarized as a reference to the experimental program. The summary includes coal composition and analysis, separation of coal macerals, relationship between coal characteristics and coal liquefaction behavior, and selective preparation of coal.

Liquefaction Process Research/Technology Development

Advanced Coal Liquefaction Catalyst Development — Amoco Oil Company

Two-stage thermal/catalytic runs using both Illinois No. 6 and Wyodak coals were continued during this period. The thrust of the program was to duplicate the encouraging results obtained in the initial two-stage tests and to explore other operating parameters.

The Illinois coal work has been centered around checking the effects of coal space velocity and lower hydrotreater temperature. Preliminary results indicate that in the ranges checked, neither parameter has a significant effect on yield and product quality. A run to check the effect of a higher dissolver residence time at a lower temperature (same severity) is presently under way.

For Run 51163 with Wyodak coal, the dissolver (first stage) space velocity was lowered to duplicate the conditions of the successful run (51154) with Illinois No. 6 coal. At this condition, a slightly lower THF-soluble conversion was obtained.

A Ni/Mo catalyst has been used for all two-stage runs. For Wyodak coal, the results with Ni/Mo in the two-stage process show marked improvement over single stage with Co/Mo catalysts. Shell 324 catalyst will be compared to the Amocat 1C. Other commercially available catalysts will be tested and also compared to Amocat.

A 30-day demonstration run with Illinois No. 6 coal at best test conditions and recycling of process-derived solvent is planned for the next quarter. Amoco is also presently investigating the possibility of conducting a 12- to 15-day demonstration run in a continuous bench-scale unit. It will be necessary to subcontract this work out to another research firm that has this capability.

Development of Significantly Improved Catalysts for Coal Liquefaction and Upgrading of Coal Extracts — American Cyanamid Company

The major effort of this quarter continued to be the operation of the Continuous Stirred Reactor

(CSTR). Some preparation and screening of new beaded catalysts, using recent formulation modifications, was also accomplished. Six experimental beads were tested in the CSTR this quarter, bringing the total to ten beads tested on Illinois No. 6 coal.

Catalyst performance is assessed on the basis of the THF-Toluene-Pentane conversions and heteroatom removal. Results are then compared to the base-line catalyst Amocat 1A.

Although the initial activity of the beaded catalysts did not exceed Amocat 1A, many of them maintained their activity (pentane solubles) better than Amocat 1A over the course of the four-day run. Some of the beaded catalysts showed no aging, as indicated by sulfur removal and toluene-soluble conversion over the course of the run. This may be significant because many of the experimental beads have lower metals loading than Amocat 1A.

Work with Wyodak coal is now underway. Six runs will be made using Wyodak coal. These will include a thermal base line, Amocat 1A base line, and four experimental beads.

After the Wyodak coal, testing of Wilsonville Illinois No. 6 coal extract from Run 245 will begin. Eight extract runs are planned and some of these may be devoted to Wyodak extract from the present Wilsonville run.

A four-month no-cost contract extension has been requested by, and granted to, American Cyanamid. Experimental work will be carried on until the end of this calendar year. The balance of the contract (February 28, 1985) will be spent in preparation of the necessary reports.

Supercritical Extraction of Coal — Gulf South Research Institute

Research during this quarter was directed toward the evaluation of the effects of liquefaction variables (temperature, residence time, and solvent density) on the extraction of Illinois No. 6 and Wyodak coals. Using ammonia as the base-line extraction fluid, runs with Illinois coal were conducted over a temperature range of 28°C to 402°C, a density of 0.212 g/cc to 0.45 g/cc, and a residence time of 0.25 hr to 24 hr. Wyodak coal tests were run over the range of 26°C to 407°C, 0.242 g/cc to 0.53 g/cc, and 0.125 hr to 24 hr. For both coals, extraction temperature changes produced the most significant effects on coal extrac-

tion. While temperature was the most important variable studied with respect to amount of extract produced, the experimental results also demonstrated that the use of polar nucleophilic compounds as supercritical extraction fluids is of key importance. In comparison with published information, ammonia provides higher conversions than those reported for chemically inert, non-polar, non-nucleophilic fluids under similar supercritical extraction conditions.

From elemental analysis results on Illinois No. 6 coal and the products of its extraction, the supercritical extraction results show that ammonia removes approximately 95% of the total sulfur content of the coal, which implies that the ammonia attacks both inorganic and organic sulfur in the coal.

During the next reporting period, the use of ammonia as a supercritical extraction fluid will be extended to the application on a North Dakota lignite. For comparison, vacuum pyrolysis runs will be completed on each coal under similar reaction and product analysis conditions. Additionally, more detailed chemical analyses on ammonia extracts will be conducted. Heavy hydrocarbons will be collected and will be subjected to GC/MS analysis. These analyses will be conducted on oil, asphaltene, and preasphaltene fractions from selected tests. A second (aliphatic amine) solvent will be selected for use in the second phase of supercritical experiments.

Carbon-Supported Liquefaction Catalysts — Pennsylvania State University

Batches of glassy carbon supports for use in catalyst studies during coal liquefaction were prepared using a procedure based upon furfuryl alcohol polymerization. Support batches were prepared in duplicate to check for reproducibility. The prepared glassy carbons are being characterized for surface areas, pore volumes, and pore size distributions.

Composite supports were also prepared using carbon black and furfuryl alcohol mixtures. These support materials are also being characterized for surface areas, pore volumes, and pore size distributions.

A continuous-flow reaction system with operating parameter limits of 500°C and 2000 psig has been assembled for evaluation of carbon-based catalysts for coal liquefaction. The system has the capability of simultaneous addition of

four gas streams or two gas and two liquid streams. The reaction system also includes the capability of operation with fixed-bed reactors of 0.5-inch and 1.0-inch diameters or with a modified Berty reactor incorporating high internal recycle rate capability. Two separate on-line gas chromatographs can be used for reactor effluent monitoring. Facility commissioning and software development for data handling are currently under way.

Characterization of Coal-Derived Components — University of Wyoming

Hydroxyl-aromatic fractions had previously been obtained from the oil and asphaltene portions of Wyodak and Kentucky 9/14-derived residual material. These four fractions were further separated into monohydroxyl and dihydroxyl components using a μ -Bondapak NH₂ chromatographic column. The following mobile phases were used to achieve the desired separation:

Monohydroxyl aromatics from oils — 95:5 of chloroform: 2-propanol

Dihydroxyl aromatics from oils — 75:25 of chloroform: 2-propanol

Monohydroxyl aromatics from asphaltenes — 95:5 of chloroform: 2-propanol

Dihydroxyl aromatics from asphaltenes — 75:25 of chloroform: 2-propanol

The resultant eight materials were characterized in greater detail using field-ionization mass spectrometry (FIMS) to obtain a better description of the composition of the fractions.

The FIMS spectra from the oils are simpler than the spectra from asphaltenes; however, additional time will be needed to interpret the spectra. The monohydroxyl and dihydroxyl aromatic spectra from asphaltenes are particularly complex. The average molecular weight for the monohydroxyl aromatics in the asphaltenes from Wyodak resid is 571; and for dihydroxyl aromatics in asphaltenes, it is 555. In contrast, the average molecular weight for monohydroxyl aromatics in the oils from Kentucky resid is 496; and for dihydroxyl aromatics in oils, it is 503.

Work is continuing with the HPLC reversed-phase separation of monohydroxyl aromatics from oils and asphaltenes. It is now possible to obtain reversed-phase chromatographic profiles

of monohydroxyl aromatics in oils and asphaltenes. This analytical approach will allow a general comparison to be made among monohydroxyl aromatics. Experiments are being performed so that some of the monohydroxyl aromatic fractions from the HPLC reversed-phase separation step can be submitted for field-ionization mass spectral analysis.

Recycle Slurry Oil Characterization — Conoco, Inc.

Samples produced by Lummus in their Bloomfield LC-Fining Facility were used to investigate the relationship between LC-Finer operating conditions and product solvent quality. The 650°F + fraction of the LC-Finer product was tested for its solvent properties using the Short Contact Time (SCT) microautoclave test. The LC-Finer runs at Lummus used deashed SCT product made from Illinois No. 6 coal, and they were made in a continuous unit with two 250-mL autoclaves in series. The LC-Finer variables of temperature (in each of the two stages), liquid space velocity, gas feed rate, and catalyst age were studied.

The process variables and various combinations of the variables were tested to evaluate the potential for developing a statistical model for the LC-Finer product solvent quality. Ten terms for possible inclusion in a model were evaluated in a stepwise regression analysis on solvent quality test data. A five-term model was selected as giving the best correlation. The key model variables were temperature (°F), catalyst age (lb 850°F + /lb catalyst), and LHSV (volume 850°F + /volume catalyst/hr); and the five correlating terms are T_1^2 , T_2 , T_2^2 , catalyst age, and $T_2 \times \text{LHSV}$. Comparison of observed versus calculated conversion (solvent quality) showed that the following correlation produced a very good fit to the experimental data:

$$\text{Conversion} = -2534.5 - 0.0487 (T_2 \times \text{LHSV}) - 0.004738 (\text{Catalyst Age}) + 7.14 (T_2) - 0.00473 (T_2)^2 - 0.0000902 (T_1)^2$$

The $T_2 \times \text{LHSV}$ term's importance is dominated by the LHSV value, and a model with only LHSV in place of the $T_2 \times \text{LHSV}$ term produced almost as good predictions.

Hydrogen consumption was also modeled to determine its relationship to solvent quality. The modeling procedures and the regression analyses used were identical to those used for solvent quality, except that hydrogen consumption (as determined from Lummus's material balances) was used as the dependent variable. The follow-

ing correlation produced the best agreement with experimental data:

$$\text{H}_2 \text{ Consumption (scf/bbl)} = -7521 - 3.23 (T_2 \times \text{LHSV}) + 9.69 (T_1) + 0.1473 (\text{Gas Rate, scf/hr/bbl}) + 0.00314 (T_2)^2 + 0.1955 (\text{Catalyst Age})$$

Based upon the completed modeling studies, the following conclusions were generated:

- The quality of the solvent produced by the Bloomfield LC-Finer can be predicted based on reactor temperature, LHSV, and catalyst age.
- Over the range studied, gas feed rate has no significant effect on solvent quality.
- Variable importance with respect to solvent quality effects decreases in the order $\text{LHSV} > T_2 \approx \text{catalyst age} > T_1$.
- Solvent quality is maximized when reactor stages are operated at two different temperatures ($T_1 = 700^\circ\text{F}$; $T_2 = 750^\circ\text{F}$ to 755°F). For reaction stages at the same temperature, $T_1 = T_2 = 740^\circ\text{F}$ is optimal.
- Hydrogen consumption can be predicted from reactor temperatures, LHSV, catalyst age, and gas feed rate.
- Variable importance with respect to hydrogen consumption decreases in the order $\text{LHSV} > T_1 > \text{gas feed rate} > T_2 \approx \text{catalyst age}$.
- LC-Finer operation at $T_1 = 700^\circ\text{F}$ and $T_2 \approx 755^\circ\text{F}$ provides good solvent quality at high conversion and moderate hydrogen consumption.

Chemistry of Extraction Phase of Two-Stage Liquefaction — Mitre-Rockwell

The purpose of this research is to perform detailed examination of the chemistry of coal interaction and product formation from first-stage operations.

The phenol- BF_3 depolymerization reaction has been applied in an attempt to determine structural changes that occur during the first stage of liquefaction in the integrated two-stage liquefaction process. Modification of the original depolymerization reaction is under way in order to develop quantitative measures of the cross-linking bridges in coal and in liquefaction residues. Initial experiments were performed using 3-fluorophenol instead of phenol. Incorporation of phenol in the depolymerization products was followed by elemental analysis for fluorine. A substantial increase in the benzene and tetrahydrofuran extraction yields was found when the liquefaction feed

coal was depolymerized with 3-fluorophenol-BF₃. The fluorine contents of the extracts indicates a substantial amount of phenol was incorporated. Analysis of the extracts by NMR is now under way.

Other experiments have been directed toward evaluation of process solvents generated during operation of two-stage liquefaction. Catalytic dehydrogenation has been adopted as a method to determine the quantity of reactive hydrogen available in the solvent. Model compounds and a mid-distillate cut of a process solvent have been dehydrogenated over a palladium catalyst. Up to 91% of the expected theoretical yield of hydrogen was recovered from dehydrogenation of tetralin in boiling durene. Evolution of hydrogen from the process solvent was slow. Approximately 10% of the hydrogen content of the sample was released after 5 days in boiling quinoline over the catalyst. The rate of hydrogen evolution was much slower but still significant at the end of the 5-day test. Improvements to the dehydrogenation apparatus are being made to provide a continuous record of hydrogen evolution in an effort to detect changes in the rate that may indicate the onset and conclusion of the dehydrogenation of specific types of compounds in a process solvent.

Refining and Upgrading

The goals of this technological area are to evaluate experimentally the applicability of conventional petroleum-processing technology for refining of coal liquid into usable fuels; to research, develop, and evaluate those refining and upgrading techniques necessary to prove the technology of coal liquids' processing; and to produce and test refined coal liquids for their applicability and capability with conventional fuels.

Refining and Upgrading of Syntfuels — Chevron Company

The objective of this program is to determine the feasibility and to estimate the costs of hydroprocessing synthetic crude feedstocks to distillate fuels using modern commercial petroleum-processing technology. Tests are conducted only to the extent needed to enable making reasonable estimates of commercial plant performance and only to the extent a commercial plant is feasible using presently existing technology, subject to the mutual agreement of DOE and Chevron Research. Tests are made for each whole synthetic oil and, if appropriate, for the fractions derived therefrom. Tests will not be

carried out for processes that can be estimated reliably.

Work during this quarter focused on Task 12, which involved the Upgrading of Integrated Two-Stage Liquefaction (ITSL) product into distillate fuels using modern petroleum-processing technology. Studies are continuing of the effect of ITSL syncrude end point on hydrotreating severity necessary for downstream refining to distillate products.

Task 12 - Upgrading of ITSL Product

A. Feeds

The ITSL process development unit at Lummus has been operated to produce net liquid products with an end point ranging from about 650°F to about 850°F. Earlier, an extensive laboratory program was conducted to upgrade ITSL oil with an end point of about 750°F. Lummus recently provided Chevron with a higher end point (800°F) ITSL oil for additional testing.

Both the new oil and the earlier sample were derived from Illinois No. 6 coal, Burning Star Mine.

According to the distillations by both Chevron and Lummus, the new sample of oil contains 27 LV (Liquid Volume) % to 28 LV % of 650°F+ material in contrast to 16% to 17% with the previous feed. The end point is over 800°F, at least 50°F higher than previously.

The distillation curves of the two oils show the shape of the curve for the new sample is rather unusual. It contains very little naphtha boiling below 350°F and a surprisingly large amount of a fraction boiling at about 375°F to 400°F. But only a small fraction boils between 400°F and 500°F.

In addition to the end-point difference, another variable in the liquefaction process may affect the quality of the oil. The new sample was produced near the end of the liquefaction run. In contrast, the previous sample was produced near start of run.

The new sample contained some water and particulates. The water was allowed to settle to the bottom of the barrel; then the oil was decanted and filtered through a 1-micron filter to remove the particulates.

The inspections before and after decanting and filtering were compared to those of the previous, lower-end-point oil. The new sample contains more heteroatoms, more metals, more hot heptane insolubles, and more Ramsbottom carbon than the other. It is also lower in hydrogen con-

tent. It is expected that all of these properties, together with the higher end point, will make the new oil more difficult to upgrade. It contained only 4 ppm chlorine, so it was not water-washed before using it as a pilot plant feed.

B. Hydrotreating of High-End-Point ITSL Oil with ICR 106 Catalyst; Pilot-Plant Run 90-171

A 1080-hr pilot-plant test was made (Run 90-171) in which the high-end-point ITSL oil was hydrotreated with ICR 106 catalyst. The purpose was to find out how well ICR 106 performs compared to its performance when hydrotreating the lower end point oil.

The catalyst for the run had been used for 1250 hr in a proprietary test (paid for by Chevron) in

which petroleum vacuum gas oil was hydro-treated. The catalyst had essentially fresh activity, although it was stable and had not fouled. The feed was switched to ITSL oil, and the test for DOE was started without interruption.

Initial test conditions for ITSL oil were the following:

Liquid Hourly Space Velocity (LHSV),
vol feed/vol catalyst hr 0.5
Hydrogen Partial Pressure, psia 2300
Total Pressure, psig 2500
Recycle Gas Rate, scf/bbl 8000

Catalyst temperatures were adjusted to make product with varying amounts of nitrogen, as shown in Table 3.

Table 3.

<u>Run Hours</u>	<u>Avg. Catalyst Temp., °F</u>	<u>Whole Liquid Product Nitrogen, ppm</u>
1250-1392	705	2.7 -3.0
1392-1420	715	Not Lined Out
1420-1830	720	0.35-0.40
1830-2330	750	0.10-0.15

At 720°F average catalyst temperature (0.35 ppm nitrogen), the product contained about 20% aromatics in the whole liquid product. In comparison, the lower boiling feed made product with only 10% aromatics at 710°F, which was 10°F lower. Clearly, the higher boiling feed is harder to hydrogenate.

Based on extremely limited analytical information, the aromatics appeared to be concentrated in the heavier fraction. In a single analysis, the jet product has a smoke point of 20, which meets specification.

The temperature was further increased to 750°F. The product nitrogen dropped to 0.1 ppm, about the limit of our ability to measure.

The product still had some color (light green), indicating appreciable quantities of aromatic compounds were still present. Analyses for aromatics are in progress.

C. Hydrocracking of Hydrotreated ITSL Oil; Pilot-Plant Run 62-281

A second-stage hydrocracking pilot-plant test was made (Run 62-281) using Chevron's commercial ICR 202 catalyst. The feeds were hydrotreated

ITSL oils, derived from the first (lower-end-point) sample from Lummus. Tests were designed to (1) make naphtha as the sole liquid product and (2) make both naphtha and jet fuel products.

Feeds of two different boiling ranges were tested: (1) 350°F + hydrotreated oil and (2) full-boiling-range (whole) hydrotreated oil.

The first 1264 hours were made with hydrotreated 350°F + oil. It was prepared in Pilot-Plant Run 86-75, described in our October-December, 1983, Quarterly Report. The 350°F- naphtha was removed by distillation. [Commercially, the 350°F + distillation oil would be second stage (hydrocracker), and the column is located between the first stage (hydrotreater) and the second stage.] Product from both stages would be fed to this column. This configuration is called "intermediate distillation." In the laboratory, the first- and second-stage tests were made separately, and the feed to the second stage was distilled prior to the test.

At hour 1264, the feed was changed to full-boiling-range hydrotreated ITSL oil, and the remainder of the run was made using this type of feed. Two different blends were composited from

product made in Pilot Plant Run 90-167. These feeds contained the 350°F- naphtha, as well as the 350°F + fraction. They simulate the hydrotreated product fed to a second stage in the hydrocracking configuration called "tail-end distillation." The entire hydrotreated liquid product from the first stage is fed to the second stage. The feed now contains material that does not have to be cracked (referred to as "overlap"), and the apparent conversion is higher than if it were not there.

All the hydrocracking tests were made in the "extinction-recycle" mode. In this mode any product boiling above the Recycle Conversion Point (RCP) is recycled back to the hydrocracker. Thus, completed conversion to product boiling below the RCP is ultimately achieved.

The conditions for the tests were the following:

LHSV, vol feed/vol catalyst/hr 1.1
 Hydrogen Partial Pressure, psia 2000
 Total Pressure, psig 2300
 Recycle Gas Rate, scf/bbl 5600

Table 4 summarizes variations in target RCP, ranging from 350°F to 550°F. The apparent per-pass conversion (PPC) ranged from 60 LV % to 85 LV %. These conversions were not corrected for overlap in the feed.

The table also gives conversions that have been corrected for overlap by the following calculation:

$$\text{Corrected Conversion} = (X - X_o)/(1 - X_o)$$

where

X = Apparent PPC Below RCP

X_o = Fraction of Total Feed (Fresh + Recycle) Boiling Below RCP (Overlap) • (Apparent PPC)

Between hour 350 and hour 1264 (with 350°F + feed), the catalyst deactivation rate is essentially linear at 0.023°F/hr.

Between hour 1264 and hour 2385 (with full-boiling-range feeds), the deactivation rate was somewhat lower — about 0.016°F/hr. (This result was calculated from the 1264-1408 hour period and 2224-2385 hour period tests at 350°F RCP. The feeds weren't exactly the same, so a small correction was applied for the differences in overlap.)

D. Program

Pilot-plant tests are now complete with Illinois ITSL oil. During the next month, much of the analytical work will be completed. A modification was made to the existing contract to facilitate the enhancement of current ITSL upgrading and refining work to incorporate a subbituminous as well as the current bituminous-derived synthetic crude. Lummus has also provided Chevron with 2 barrels of ITSL process product derived from subbituminous Wyodak coal.

The ITSL engineering studies will be made after the experimental work is complete. Interim Report No. 9 describing Exxon Donor Solvent oil was completed and is designated DOE Report No. DOE/ET-10531-T19.

Table 4.
Pilot-Plant Run 62-281; Summary of Conditions

Run Hours	RCP, °F	PPC Below RCP, LV %		Average Catalyst Temperature, °F
		Apparent	Corrected	
0-1264	450	60	59	560-590
1264-1408	350	68	65	592
1408-1548	400	80	75	591
1548-1718	450	83	77	583
1718-1834	500	83	73	578
1834-1906	525	85	73	577
1906-1964	535	81	67	576
1964-2224	550	78	59	568
2224-2385	350	64	61	606

Indirect Liquefaction Projects

The overall objective of this activity is to develop, implement, and manage indirect coal liquefaction industrial research and development (through PDU scale) projects for expanded use of coal as a petroleum substitute. The specific goals of this technological area are to perform research studies and bench-scale/PDU process evaluations for the development of viable methods to convert synthesis gas into needed liquid fuels and to improve the activity, selectivity, and efficiency of such processes.

Liquid Phase Methanol PDU Program — Air Products and Chemicals, Inc.

The objective of this project is to demonstrate the technical feasibility of the Liquid Phase Methanol Process (LPMeOH) at the PDU scale. Indirect coal liquefaction is a promising way to convert coal resources into clean, liquid fuels such as methanol. The LPMeOH technology is particularly suited for integration with coal-based syngas processes and has the potential to be a more-efficient, lower-cost, conversion route to methanol.

Phase III and Phase IV tasks are now the focal point of the program for this quarter. Specific tasks included Task 6, Liquid Fluidized Operation; Task 7, Laboratory Support Program; and Task 11, Project Evaluation and Reporting. Activities associated with each task were completed as follows:

Task 6 - Liquid Fluidized Operation

● Field Engineering

The LaPorte LPMeOH PDU was restarted after the successful 10-day shakedown run completed in March. Thirteen hundred fifty lbs of EPJ-19 catalyst were loaded into the reactor on April 5 and 6. After reduction and bed expansion testing, balanced gas was fed, and methanol was first made on April 11. As with the first run, the pelletized catalyst rapidly attrited to a fine slurry, resulting in a 27-wt% to 28-wt% (as oxide) slurry. Nonetheless, the catalyst remained highly active, as an 8-tpd rate of methanol production was maintained from April 12-14 with a balanced feed gas.

On April 15, reactor feed was changed to a CO-rich gas, and process conditions were established for the remainder of this extended run. Mechanical performance of the PDU was excellent throughout the run; however, an absolute decline in methanol production was observed.

Much of this decline can be attributed directly to a decreasing catalyst inventory throughout the run, due to accumulation on vessel walls in the slurry loop and carry-over to the product recovery system. When corrected for this effect, catalyst productivity can be demonstrated to have declined at an approximate 1.1% per day rate. Again, this is greater than experienced in laboratory units; but, plausible estimates of the effect of carbonyls narrow the difference.

Following the run termination on May 21, a careful inspection of the unit was made to account for the catalyst inventory losses implied by nuclear density gauge readings on the reactor, the running oil inventory table, and the final inventory reading made by direct level measurement at the end of the run.

Task 7 - Laboratory Support Program

● Miscellaneous R&D Support

Autoclave Tests of the LaPorte Catalyst Used in the Shakedown Run

The EPJ-19LR catalyst used in the shakedown run was considered for reuse in the subsequent 40-day run. In addition to analyses of the used catalyst, an activity test was felt necessary to ensure the success of the 40-day run.

At the end of the shakedown run (248 hours on syngas), the catalyst slurry was transferred into the slurry prep tank (28.30) ready for the next activity maintenance run. A slurry sample taken from the prep tank was filtered and then washed. The catalyst was submitted for ESCA and XRD. An unusual phase was detected on the catalyst. This sample was from the bottom of the tank just above the valve. It was speculated that the phase could be $2 \text{ Al}_2\text{O}_3 \cdot 5 \text{ ZnO} \cdot 18 \text{ H}_2\text{O}$, leading to a conclusion that a small quantity of water might have been present in a pocket above the valve.

Another slurry sample was taken from the bulk of the prep tank. After confirming this sample was "normal" by XRD, the sample was charged in the 300-cc autoclave and tested on CO-rich gas. A heater malfunction prevented achieving 250°C in the autoclave, and instead, 225°C was selected. The MeOH productivity and CO conversion were plotted with time. Both indexes are significantly lower than what would be expected of fresh catalyst (12.5 MeOH mol/hr-kg of catalyst and 11% CO conversion). Moreover, a rapid decline in MeOH productivity and CO conversion was taking place with time. The productivity decline for this 225°C run was five times as rapid as for a previous

autoclave run at 250°C. There clearly was something wrong with the slurry, and the decision was made not to use it in the 40-day run to follow.

It was still of interest to determine why the catalyst performance in the autoclave was so poor. Several hypotheses were proposed. The catalyst could have been contaminated during the transfer into the prep tank, which may have contained some water or Metex solution in spite of all the cleanup prior to the slurry transfer.

Another sample was requested from the LaPorte prep tank. Great precautions were taken for this sampling. A special stainless steel sample bomb was fabricated, cleaned, and purged with N₂ and filled with the slurry. The container was sealed tight and transferred to our laboratory. Elaborate precautions were taken in weighing out the slurry into the autoclave under N₂ atmosphere. A sample was also sent for analysis. The analysis of oil showed it to contain 1852 ppm of iron, which is significantly higher than the 830 ppm iron observed in oil from the process loop at the end of the shakedown run. The MeOH productivity and CO conversion were plotted with time. The rapid decline in MeOH productivity is still observed. The CO conversion data, however, show substantial scatter and a possible decline as well. The run was terminated when it became obvious that both indexes were less than 50% of those of a fresh catalyst. The sample from the autoclave was analyzed and compared with results of the shakedown oil sample. The Fe content was high, as noted in oil from the autoclave test. The Ni content was higher, leading us to conclude that some Metex solution had most likely been left over in the prep tank even after the cleanup. The minor changes in crystallite size, Cu/Zn ratio, and Cu⁺/Cu⁰ ratio between oil samples used do not explain the rapid decline in activity during the autoclave run.

In summary, it was a good decision not to use the LaPorte shakedown slurry for the 40-day run. The slurry performance was substantially lower than that of a fresh catalyst. Its activity maintenance in the autoclave was poor. It is believed that one of the causes may be the contamination of the slurry with traces of Metex solution when it was transferred into the prep tank for storage.

Catalyst Analyses for the LaPorte 40-Day Run

The durability of catalyst activity under typical operating conditions has significant impact on the LPMOH process technology. Steady activity decline observed in the lab autoclave (as discuss-

ed in the previous section) using slurry samples taken from the shakedown run highlighted the concerns over catalyst deactivation. A very extensive program was committed to monitor the state of the catalyst and the extent of poisons' pickup during the 40-day run.

Slurry samples (catalyst fines in oil) were taken from the circulation loop after the slurry pump at various stages of the PDU operation. To avoid air contamination, each sample was blanketed under N₂ pressure and transferred to APCI Allentown facilities via courier services for catalyst analyses. Twenty-one samples were shipped. Each slurry sample was first filtered and then thoroughly washed with cyclohexane to remove residual oil on the catalyst before submittal for analyses.

Some interesting observations can be made. The Cu/Zn and Cu⁺/Cu⁰ ratios changed radically in transition from balanced gas to CO-rich gas (after 130 hours on-line). It is quite amazing to see (1) "surface" (20 Å) Cu/Zn ratio reduced to less than 0.1 when the bulk composition of the catalyst has a Cu/Zn ratio of approximately 1.5, and (2) Cu⁺/Cu⁰ dropped to nil at the end of the run despite the fact that the catalyst was still active.

Copper crystal size was noted to grow with time on stream. The step change from 96Å to 166Å in the first few hours on syngas is surprising. Perhaps the mechanism of attrition precipitated this phenomenon. Trace analyses of the catalyst samples show increases in iron and nickel consistent with carbonyl surveys in the reactor feed gas. Chlorine and sulphur pickup did not appear to occur over the run. Carbonyl surveys across the plant confirmed a slow buildup of nickel in the gas entering the reactor. The primary source was tracked down to the feed gas compressor, and subsequent inspection after the run revealed approximately one pound of Raney Ni catalyst in the compressor inlet filter. A slow but steady buildup of iron and nickel is apparent and must have taken its toll on catalyst performance.

Task 11 - Program Evaluation

Carbonyl Survey During LaPorte Shakedown Run

An intensive survey of iron and nickel carbonyls was conducted during the LaPorte shakedown run to determine the magnitude of carbonyls in the feed gases to the reactor. Particular attention was given to vessels and piping made from materials (carbon and carbon-1/2 Mo steels) suspected of generating carbonyls.

On balanced gas, no carbonyl levels were observed above the detection limit of 10 ppbv. On CO-rich gas at 50,000 scfh reactor feed (482°F, 750 psig reactor conditions), carbonyl levels were very low. The primary sources of iron carbonyl formation were the shell-side pass of the 21.10 exchanger (reactor-feed side), and the tube sheets and exchanger heads (carbon-1/3 Mo) on the 21.20 tube-side section (reactor effluent side). Nickel carbonyl levels were very low and consistent with cleanup of residual nickel contamination in the recycle line, which could not be treated chemically during the Metex wash. At higher gas rates, all carbonyl levels were below the detection limit.

In conjunction with the carbonyl survey, a carbon adsorption test was conducted to determine the effectiveness of activated carbon (Calgon BPL) in removing carbonyls. A side stream of the reactor feed gas, which contains methanol and oil vapors, was passed through a 1-inch-diameter x 1-inch-long carbon bed. Carbonyl levels in the inlet and outlet of the bed were determined as a function of time. Because the carbonyl levels during the run were very low, accurate determination of the adsorption capacity was difficult. Qualitatively, carbonyl breakthrough was observed early in the test, and methanol/oil breakthrough indicated that during PDU operation a carbon guard bed would be saturated with organics quickly. The test results suggest a carbon system would have limited effectiveness for removing carbonyls at the low levels observed in the LaPorte PDU.

Carbonyl Measurements During LaPorte 40-Day Run

Carbonyl surveys of the PDU were made during the 40-day run at LaPorte to determine the carbonyl formation during long-term CO-rich operation. The first survey was undertaken in the early part of the run on CO-rich gas (150 hours cumulative run time, 50 hours on CO-rich gas). Carbonyl levels in the plant were all below the detection limit. These levels, at 100,000 scfh gas rate, are consistent with the levels at high gas rates in the shakedown run. The initial high nickel carbonyl concentrations in the 27.14 effluent were attributed to sample system contamination.

A second survey was conducted in the middle of the run (650 hours cumulative run time, 550 hours on CO-rich gas). The detection limit for analysis was improved, and a steady low level of iron carbonyl of 6 ppbv was observed. This level is comparable to the slow buildup of iron seen on the catalyst. Nickel carbonyl levels of finite value were first observed in this second survey; $\text{Ni}(\text{CO})_4$

was detected at 20 to 40 ppbv in the outlet of 01.13 and the reactor feed. A third carbonyl survey was made to determine the source of $\text{Ni}(\text{CO})_4$.

● Summary

This quarter, the Liquid Phase Methanol Program was highlighted by the successful operation of the LaPorte PDU in conducting the 40-day activity maintenance run using the EPJ-19LR catalyst. Operation was smooth, and the post-run inspections showed that the plant was in good condition, free of blockages or large deposits. However, about 20% of the original catalyst charged had deposited as film on vessel walls or in dead spaces. Catalyst activity declined slowly over the run, dropping at a rate of 1.5% per day relative to methanol productivity. The methanol production decreased from an initial 5 tpd to a final 2.5 tpd. The rate of deactivation, considering catalyst loss and carbonyl exposure, remained somewhat higher than achieved in the laboratory reactor. The 40-day run produced 165 tons (50,000 gallons) of methanol.

Valuable information on catalyst activity maintenance, as well as on changes in catalyst properties such as crystal size and $\text{Cu}^{+1}/\text{Cu}^0$, was obtained.

Based on the slurry inventory measurements and the slurry concentration determined by the nuclear detector gauge, it was estimated that 273 lbs of reduced catalyst were "lost" during the run. This agrees very well with the 286 lbs (25%) catalyst recovered or accounted for in the post-run inspection. When the decreasing catalyst inventory is considered, the catalyst productivity per unit catalyst mass declines at a rate of approximately 1.1% per day. The rough estimate of the effect of carbonyls has suggested an incremental loss on the order of 0.3% per day.

The mechanical performance of the LaPorte PDU during the 40-day run was excellent. With almost 1000 hours of slurry operation, there were no signs of erosion of the slurry pump or piping. The Stein seal functioned extremely well. After the unit was inspected, it was cleaned out and prepared for the next run.

The contract was modified to conduct a liquid-entrained run using a commercial powdered catalyst, namely, BASF catalyst No. S-385. Elements of the run included PDU preparation, in situ reduction with 5 days of balanced gas operation. This run was begun June 11, 1984, and was completed on June 21, 1984. Results from these operations will be included in the next quarterly report.

Industrial Technology Projects

Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels — Mobil Research and Development Corporation

The objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H_2/CO ratio synthesis gas into maximum yield of gasoline and distillate transportation fuels. The work performed under this contract includes the demonstration of long-term, stable operation of the bench-scale unit under conditions of low fuel gas — high reactor wax production, the collection of processing data for upgrading Fischer-Tropsch wax to diesel oil, and the operation of hot, nonreacting bubble-column reactor models to obtain hydrodynamic scale-up data.

Evaluation of a new Fischer-Tropsch catalyst I-D ($Fe/Cu/K_2CO_3$) continued in the two-stage bench-scale pilot plant. Stable low methane and ethane operation was demonstrated over the entire run length. Addition and in situ activation of fresh Fischer-Tropsch catalyst were also demonstrated. The run was terminated after 33 days because of a substantial loss of activity after three-day N_2 purging at $250^\circ C$.

A 0.5-mm 3-hole distributor was studied in the 5.1-cm-i.d. x 9.1-m-tall hot-flow bubble column using a Fischer-Tropsch-derived paraffinic wax. The gas holdups and bubble flow patterns were similar to those using a 1-mm orifice reported earlier. Also, scoping hydrodynamic studies in a 5.2-cm-i.d. x 2.1-m-tall hot-flow bubble column indicate that orifice-type distributors that produce the same gas-jet velocity produce similar holdups.

Air Products F-T Slurry

Slurry tests on modified conventional catalysts have been continued with testing of two new compositions.

The effects of promoter loadings on the slurry phase activity and selectivity of a series of coprecipitated catalysts have been investigated. Significant increases in bulk activity and marked changes in selectivity have been observed.

The effect of catalyst pretreatment on activity and selectivity was investigated via slurry tests of coprecipitated catalysts. Pretreatment conditions significantly affect the product selectivity.

The effects of activation methods on performance of a coprecipitated catalyst were investigated in the gas phase. Activation routes tested include (1) activation in syngas, (2) reduction in H_2 ,

and (3) reduction in H_2 followed by carbiding in CO. Bulk activities were similar in all cases, with only small variations in selectivities.

A statistical correlation has been developed for gas holdup data obtained from the 12-inch cold-flow simulator. Gas holdup has been correlated with four parameters: gas velocity, slurry density, distributor hole size, and liquid velocity. Gas velocity and slurry density have the largest effect on gas holdup.

The optimum gas holdup as a function of catalyst activity, catalyst loading, bubble diameter, and gas-liquid mass transfer was calculated. As catalyst loading is increased from 20 wt% to 60 wt%, optimum gas holdup increases from 13% to 21%. To achieve holdups in this range, bubble column operation must be in the churn turbulent regime.

Liquid Hydrocarbon Fuels From Syngas — Union Carbide

The objective of this contract is the direct catalytic conversion of syngas to liquid motor fuels, including gasoline, turbine, and diesel oil, with product selectivities and quality superior to those provided by the conventional Fischer-Tropsch process. The catalysts being studied consist of a Fischer-Tropsch metal component (MC) and a shape-selective molecular sieve component (SSC) to control hydrocarbon boiling range and quality.

Remarkably stable catalysts with the metal component intimately mixed with the shape-selective component have been synthesized. One such catalyst, consisting of cobalt, thoria, UCC-101, and an additive, produced nearly 70% motor fuel (gasoline + diesel) at a syngas conversion of 75%. The catalyst lost less than 2% syngas conversion during its twelve days on stream. Almost all of the loss occurred during the first 100 hours of the run. Furthermore, this catalyst lost only 0.6% of its selectivity to motor fuels during the same period.

Achieving such unusually high stability in a cobalt catalyst indicates considerable progress towards achieving one of the primary goals of the contract.

Support Studies/Engineering Evaluations

The overall objective of this activity is to develop, implement, and manage projects that are generic in nature and applicable to all the liquefaction process technologies under develop-

ment. Goals of this technological area are to (1) develop strong supporting technology in the component and instrument areas for coal liquefaction programs through contracted projects to the National Laboratories, Universities, and Industrial Organizations, (2) conduct fundamental research in coal liquefaction, and (3) conduct technical evaluations and assessments of advanced liquefaction concepts.

Component and Instrument Projects

The goals of these projects are to (1) develop strong supporting technology in the component and instrument areas for coal liquefaction programs through contracted projects to the National Laboratories, Universities, and Industrial Organizations; (2) provide an adequate component and instrument data base for the scale-up of liquefaction processes; and (3) promote the transfer of technology. The highlights of the projects of the past quarter follow.

Centrifugal Slurry Pump Wear and Hydraulic Studies — Ingersoll-Rand Research, Inc.

The objective is to develop a data base and methods that will provide guidance to centrifugal coal slurry pump vendors and users to improve design and extend lifetime. Specifically, materials selection, wear patterns, hydraulic design, and interactions with various slurries will be treated. The project involves two main areas, namely, hydraulic studies and wear studies.

During this quarter, Ingersoll-Rand continued the development of the prototype pump, by completing the detailed design of the pump, and the construction and debugging of the test loop to shop-test the pump.

● Prototype Pump Development

The design of the main pump was reviewed with the pattern shop engineers, and several details were made final. The detailed casting and machining drawings for the internal components, such as impeller, volute liner, suction plate, and back plate, were also completed and reviewed with engineers from the foundry, pattern shop, and engineering, and quotations have been solicited. Remaining designs on shaft, casing, etc., are now being prepared and are scheduled for completion in July.

● Test Facility Development

The test loop installation was completed, and check-out of all components was begun. The components were initially operated for a short time;

and upon satisfactory check-out of each component, the test loop was operated with water at full flow and pressure. Electrical and piping components were also checked. Calibrations on booster pumps, weigh hopper assembly, pressure transmitters, and other instruments were also performed. Several modifications were made on one of the pump drive mechanisms and on the bucket elevator. Once the water check-out was completed, check-out with sand-water slurry was repeated. The debugging of the test loop has been completed, and the reciprocating pump developed under another contract to Ingersoll-Rand can now be shop-tested.

● Comparative Calibration Testing of Prototype

A state-of-the-art pump from a coal liquefaction facility has been secured, and refurbishing of the pump for comparative erosion tests with the prototype pump has begun.

● Phase II Report

The final phase II report, detailing the basic developmental approaches, such as the development of the basic mathematical wear model relating pump life to some of the key design and operating parameters, and the material investigation and screening research at several laboratories, has been issued during this quarter.

Development of a Synthetic Fuel Reciprocating Charge Pump — Ingersoll-Rand Research Inc.

The objective of this project is to improve the performance and reliability of the reciprocating slurry pump by isolating the trouble-prone stuffing box from erosive slurry by using various concepts of sealing, which may involve a seal and/or buffer fluid.

During this quarter, one of the concepts of using a twin diaphragm seal was fabricated and tested with water. The volumetric efficiency of the diaphragm seal is higher than the efficiencies of the liquid-leg and floating-piston concepts, and is about 82% at the design speed of 150 rpm. The buffer fluid volume control was tested to determine its ability to maintain sufficient level of control by inducing various modes of component failure. This testing completed the shop-test intended for the program. Since a good-size operating coal liquefaction plant is not available to perform field testing of the floating-piston seal, Ingersoll-Rand was directed to test the concept with sand-water slurry on the test loop constructed to test the centrifugal pump. The reciprocating pump has now been relocated and in-

stalled on the sand-water loop for the endurance check. Two floating pistons have been installed, and one plunger of the three-plunger pump will be operated conventionally to provide a basis for erosion study. All electrical and piping connections have been completed, and debugging has been started.

Solid/Liquid/Gas Phase-Fraction Meter — Science Applications, Inc.

The objective of this project is to develop a phase-fraction meter capable of indicating the portion of solid, liquid, and gas in weight percent of a high-pressure, high-temperature coal-liquefaction stream, typically the effluents from the preheater.

During this quarter, Science Applications, Inc. (SAI) completed the design of the spool piece and associated hardware. Fabrication of the hardware requires considerable safeguards to protect the detectors, and cooling-water coils have been fabricated inside the shielding surroundings to maintain temperature control. Because of the space limitation at the intended location at Wilsonville, the overall spool piece length has been limited to 36 inches. This space constraint requires special design to be included to minimize cross talk occurring between the electronics. The high-energy source is mounted at a 60° angle to provide a wider target area of materials flowing in the pipe, while the low-energy source is mounted next to a "window" to enhance the action of low-energy neutrons. The fabricated spool piece was successfully high temperature and pressure tested, and radiographed. The window on the spool piece requires thinning of a section of the pipe wall and thus induces concern on the spool piece's ability to sustain high temperature and pressure.

The two sources for the phase fraction meter have been ordered from Amersham Corporation. The high-energy source is a 300-microcurie ^{241}Am (300 mCi of ^{241}Am), and the low-energy source is a 10-microcurie ^{137}Cs (10 mCi of ^{137}Cs). Both sources are doubly encapsulated and certified to withstand the severe environmental constraints that are expected in the proximity of the process pipe. The source sizes were selected on the basis of required meter precision, geometrical constraints, and personnel safety.

Science Applications, Inc., estimated that the count-rate range for both gamma ray detectors will be in the range of 100,000-150,000 counts per

second in order to detect slug flow and to achieve the required precision of 0.1% in counting statistics in a 10-second cycle. This requires the use of equally fast-counting electronics. The simplest system envisaged at this time is an ORTEC Fast Filter Amplifier in conjunction with an ORTEC or Tennelec Discriminator. These count scalars are designed to perform well at these count rates and are not expected to present any problems. These will be board-mounted on the back plane of the data acquisition and analysis computer.

The on-line computer system requirements have been studied extensively, and it has been decided that a PDP-11/23 computer will be the heart of the system. The final decision on the necessary peripherals has not been made yet because SAI is trying to hold the budget line in this project.

The software design is about half complete, and the remaining programming is expected to start within the next reporting period.

Coating Studies for Coal Conversion — Oak Ridge National Laboratory

The objective of this task is to develop chemical vapor deposition coatings that extend the life of valve trim materials in coal conversion applications. Coatings are applied at Oak Ridge National Laboratory (ORNL) and are erosion-tested at Battelle Columbus Laboratories.

Current efforts are directed toward improving the understanding of the coating process and the erosion performance of coatings. During this quarter, 69 coating experiments were conducted to investigate the effect of various process parameters on coating properties and erosion performance. In addition to the variation in process conditions, several runs were made at 900°C to test different substrate materials. These substrates included standard cemented tungsten carbide, hot-pressed TiB_2 , two grades of abrasion-resistant cast iron (HC-250 and 1503), and several experimental grades of tungsten carbide.

The analysis of previously prepared coatings indicated variations in the chlorine-to-titanium ratios in these coatings (TiCl_4 is one of the reactants used in forming the TiB_2 coating). A new technique is being used at ORNL to determine the actual chlorine concentrations. Results to date indicate that coatings deposited at 800°C, 900°C, and 1000°C had chlorine concentrations of 5.72 wt%, 0.33 wt%, and 0.0 wt%, respectively. The effect of the chlorine content on erosion performance is being investigated.

Data to date also show that TiB₂ deposited at 1000°C is essentially stoichiometric (i.e., a boron-to-titanium ratio of 2.002). Coatings deposited at 900°C and 800°C have boron-to-titanium ratios of 2.006 and 2.066, respectively. The impact of the stoichiometry on erosion performance is also being investigated.

Elastomer Test Program — Oak Ridge National Laboratory

The objective of this project is to test an elastomer in an operating coal liquefaction pilot plant (Wilsonville) environment. This elastomer will be used as a seal material in pumps and valves.

This project was initiated in May 1984. Based on consultations between ORNL and the Wilsonville staff, pump P1039 was selected for initial testing of the elastomers. The typical operating-temperature range for this pump is 350°F to 450°F, and the fluid pumped is flush solvent. If the elastomers perform favorably in these tests, they will be subjected to more severe test conditions at another location.

Two suppliers were contacted to obtain test specimens of elastomers. Specimens of the appropriate size for use at Wilsonville were received. Laboratory tests in Wilsonville liquids will be performed; and after satisfactory completion of these tests, the specimens will be shipped to Wilsonville for installation.

Development of Active Acoustic Cross-Correlation for Flowmeter Calibration — Argonne National Laboratory

The objective of the project is to develop and apply the active acoustic cross-correlation technique for on-line calibration of flowmeters in coal liquefaction pilot plants. Flowmeters in these plants will need periodic on-line calibration to be used effectively in material balances and optimum control of the plants. The active acoustic cross-correlation technique will provide such a calibration device, since it is based on instantaneous disturbances in the flow and their propagation between two observed points.

In this quarter, Argonne National Laboratory (ANL) has tested the cross-correlation technique with two transducer sizes, 1/2 inch and 1/4 inch in diameter. A 15-wt% coal-water slurry (Ohio No. 9 coal) was circulated in the ANL flow calibration loop. The slurry velocity tested ranges from 0.4 to 1.4 m/s in a 2-inch line. Both sets of sensors were

installed at a vertical test line; transducers were placed 4 cm apart. The same sensing electronics were used for both systems; the cross-correlation function was calculated by the HP-5451C analyzer. The peak position of a cross-correlation function was used to compute the slurry velocity and then compared with the mean velocity obtained by the weight-diversion technique. Results indicate three significant effects due to the change of transducer size. As the transducer size is reduced, the flow-related signal decreases sharply. Thus, a poor signal-to-noise (S/N) ratio is expected. For the 1/4-inch transducer, correlation peaks were poorly resolved, particularly for low velocities (<1 m/s). Another effect that is partially related to S/N ratio is the operating frequency. For a 1-inch transducer, ANL found a wide range of frequency usable for the cross-correlation technique; the optimum frequencies are near and above 1 MHz. For the present tests, the optimum frequency for both 1/2-inch and 1/4-inch transducers is above 1.5 MHz. For any signal below 1.5 MHz, the background noise due to direct channeling through pipe wall dominates the signal and causes interference in the sharp formation of a cross-correlation peak. Another important effect in the meter design is the variation of the meter factor, which is defined as the ratio of the mean velocity and the measured velocity based on the correlation peak. In the velocity range thus far tested, the meter factor has varied from 0.8 to 0.88 for the 1/4-inch transducer system and from 0.84 to 0.9 for the 1/2-inch transducer system.

In this quarter, ANL also examined signal-conditioning electronics that will be incorporated into the integrated on-line instrument. Both AM and FM demodulation systems have been designed. Hardware required for the cross-correlator has been evaluated and screened. The core of the hardware will probably consist of an Intel microprocessor.

Development of a Continuous Mass Flow Measuring System — Science Applications, Inc.

The objective of this project is to develop a nonintrusive instrument system capable of measuring the mass flow rate of a viscous, caking coal product slurry, which is usually at high temperature and pressure besides being erosive and corrosive. The instrument system employs the pulsed neutron tracer technique to determine the time of flight of moving elements and, together with a gamma densitometer, will provide the average mass rate.

During this quarter, design work has continued on the prototype. Efforts have been made in investigating the source effectiveness, geometry, shielding, and cooling design considerations. The densitometer source-sizing calculations have been performed and the shielding requirements have been determined.

Science Applications, Inc. (SAI) initiated the screening of available neutron generators to determine the limits and advantages of each unit. Several manufacturers were contacted, and based on information supplied, SAI finds that the most suitable generator is the one that can be supplied by KAMAN. The KAMAN 711, with pulsing modifications, will provide a sufficient output of neutrons for the flowmeter, and SAI has recommended its purchase. Firm quotations have been solicited from KAMAN for the generator.

Science Applications, Inc., has also investigated the shielding problem this quarter. Issues of safety, weight, flexibility, and environments increase when a large source such as the KAMAN 711 is used instead of the smaller KAMAN 801 previously planned.

The preliminary design is for a shield 30-inches thick radially from the source, with 45 inches along the pipe plane. The plan is to make the shield as adaptable as possible to varying plant locations, including eventual use on a larger-scale plant with 10-inch piping. There will be two halves: upper shield with neutron generator module, and a lower shield assembly that goes under the pipes. Both halves will be tanks that are to be filled with water to which some neutron-absorbing compound is added; lithium and boron are under consideration.

Improvement in shield effectiveness near the generator is achieved by use of iron to act as a reflector and moderator of the fast neutrons. Water will continue the thermalization and absorb the remainder. Neutron transport calculations will be performed to choose the optimal thickness. Copper or brass are also candidates for this innermost layer. If water shielding is used next to the generator, the oxygen in water will be activated and will cause significant activation in the background. To overcome and reduce this, an 8-inch polyethylene layer is used nearest to the generator. Neutrons penetrating this layer will lose most of their energies and will be significantly below the 10-MeV threshold to activate oxygen.

Work for the next period will consist of refining the mathematical models via some experiments

with a laboratory generator and via neutron transport calculations.

Contraves Rheometer — Mound Laboratory

The objective of this project is to determine the suitability of the Contraves rheometer as a possible on-line instrument for measuring the viscosity of a viscous caking stream.

As reported in the last quarter, the rheometer has been shipped to Wilsonville but has not been installed because of the lack of capital funds at the pilot plant. Since the Fossil Energy Group at the Mound Laboratory has been dissolved, Argonne National Laboratory has been contacted to provide assistance to continue efforts in this project.

Development and Evaluations of an Abrasive Fluid Letdown Valve — Pacific Valves, Inc.

The objective of this project is to design, build, and test a letdown valve to sustain the severe environments of coal liquefaction systems. The self-impingement concept is applied to the valve design, in which the high-energy stream is separated and the parts directed at each other in order to dissipate the resulting high-rubbing energy and pressure-collapsing energy.

During this quarter, Pacific Valve began the design of the novel letdown valve with specifications developed by Pacific Valve and Wilsonville personnel. Since the Wilsonville letdown area has a low flow, it is unlikely that this particular valve can be sized down to a small size and still allow large particles to flow through. Pacific Valve and DOE are exploring alternative sites for testing of the letdown valve.

Fluid Seal Development for Coal Liquefaction Slurry Pumps — Rockwell International Corporation

The objective is to establish the technology to provide fluid seals, either hydrostatic or hydrodynamic, for reciprocal and centrifugal slurry pumps suitable for (1) coal liquefaction plant service and (2) conceptual scale-up to demonstration and commercial size in a feasible and economical form.

During this quarter, the centrifugal seal testing was begun. The centrifugal pump tester stuffing box bore required rework to correct an out-of-round condition that prevented installation of the seal housings. The pump throat bushing was reworked to increase the inside diameter to allow

for tooling to remove the seal housings from the stuffing box. Tooling was fabricated to install and remove the seals. The lantern ring was reworked to add antirotation pins. The seal housing O-ring groove was machined deeper to reduce the O-ring squeeze, and a lead-in chamber was added for installation. It was necessary to procure new O-rings for the seal housings owing to initial specification of an incorrect size.

The test facility buildup and the facility certification testing were completed. The certification testing was required to verify satisfactory facility operation prior to running the tester. The tester slurry and flush cavities were bypassed for the certification testing.

A preliminary checkout was performed by filling both the slurry and the flush systems with ambient temperature Mobiltherm 603 and then flow-through testing the system at the required conditions. The Mobiltherm 603 was then heated in both the slurry and the flush systems to verify heater operation. Satisfactory operation of the flush system was demonstrated.

The slurry system was certified by draining the Mobiltherm and filling with the slurry mixture. The slurry mixture was initially 60% coal powder by weight; however, the mixture was too thick for the mixing device and would not flow into the system. The coal powder was reduced to 50%, and the mixture was heated to 250°F in the fill tank while pressurized with gaseous nitrogen to reduce the viscosity. The slurry tanks were then filled with the 50% mixture and heated to the required 500°F. The coal powder settled to the bottom of the tanks and clogged the drain valves after sitting over the weekend. The valves were cleared with pressurized nitrogen, and satisfactory operation of the slurry system was demonstrated.

Checkout of the centrifugal seal with coal slurry at pressures of 100, 200, and 300 psig was initiated. The 100- and 200-psig 30-minute test points were completed successfully. The 300-psig test point was terminated after 9 minutes because of excessive flush seal leakage caused by metal chips caught in the seal. The seal was cleaned and reinstalled to complete the checkout testing at 300 and 400 psig. The seal performance was satisfactory. Post-test inspection of the seal indicated all hardware was in excellent condition, with no evidence of rubbing contact.

The start-up transient test series to perform 100 starts of six-minutes duration each at 300-psig slurry and 400-psig flush was begun. Four starts for six minutes each were completed successful-

ly. The seal performance was satisfactory; however, considerable difficulty was experienced with clogging of the slurry valves and plumbing. A new slurry mixing tank was installed to improve the mixing procedure and allow preheating of the slurry before transferring it into the slurry tank. The slurry flow loop will be simplified to use one line from the slurry tanks to the tester and allow the flow direction to reverse through the tester when the tanks are switched. Also, the slurry flow rate will be increased. Maintaining continuous flow at a higher velocity will minimize clogging.

During this quarter, the reciprocating pump tester was received from Ingersoll-Rand to complete the seal tester hardware fabrication. The reciprocating pump tester fluid seals were installed on the pump tester in preparation for the reciprocating seal tests. The seal installation was completed with no problems or rework. The reciprocating tester is ready for testing and will be held at Rocketdyne until the centrifugal seal testing is completed.

Correlation Examination of the Critical Solvent Deasher (CSD) Feed Quality Monitor Data — Oak Ridge National Laboratory

The objective of this program is to correlate measurements of the CSD feed quality monitor at Wilsonville with more rigorous analytical data, such as the Soxhlet assays.

In order to achieve the objective, it was necessary to persuade Wilsonville to increase the number of samplings and assays on the feed quality monitoring system. Starting this quarter, Wilsonville has implemented the increase in samplings and assays, and data have been forwarded to ORNL. During the next quarter, ORNL will receive more data from Wilsonville to perform the correlation.

Liquefaction Support Activities — Sandia National Laboratory

Investigation of the mechanisms for catalyst deactivations was continued. Catalysts deactivated in the microreactor were subjected to the same pyrene activity tests as aged catalysts from Wilsonville Run 242. Results of both tests fell on the same deactivation curve, suggesting that the catalysts had the same deactivation mode (uniform poisoning by carbonaceous deposits) and that the microreactor may be a suitable tool to study this deactivation mechanism. The rapid initial deactivation by carbonaceous deposits was also demonstrated, in that a catalyst subjected to

coal-derived feed at 400°C and 800 psig hydrogen accumulated 8 wt% carbon and lost more than 50% of its initial hydrogenation activity in just 5 minutes.

Modifications to the Helical Screw Rheometer (HSR) were completed, and gelling studies with Illinois No. 6 coal were undertaken. The HSR can now be operated with an external recirculation loop from which samples can be taken during gelling studies for subsequent chemical analysis. The coal slurry can be charged at ambient temperature and control-heated to as high as 400°C over the test period. In replicate experiments with 38.5 wt% Burning Star Mine coal and hydrogenated creosote oil at 100 psig N₂ and a shear rate of 220 sec⁻¹, a 400-centipoise increase in viscosity was observed over a 20-minute period at fluid temperatures of 300°C to 315°C.

In the Wyodak coal dissolution studies, an 80% conversion of Wyodak coal to THF solubles was achieved at 375°C for 20 minutes using naphthol as a solvent. The HPLC analysis indicated a high degree of complex formation, similar to that observed from Wyodak coal liquefaction in indole. Fourier Transform IR analysis on the isolated complexes conclusively showed the presence of extensive hydrogen bonding. This supports the hypothesis that Wyodak coal is held together by hydrogen bonds and that liquefaction in indole or naphthol disrupts these bonds through formation

of stronger coal-solvent hydrogen bonds, resulting in THF-soluble complexes.

A new procedure using high resolution gas chromatography has been developed to follow the rate of hydrogenation of individual polynuclear aromatic components of a coal-derived liquefaction process start-up solvent. The concentrations of the major components within creosote oil could be determined accurately, and several hydrogenated components appeared to approach equilibrium with their parent compound. This type of analysis could be of major benefit to rapid on-line monitoring of catalytic hydrotreater performance.

The Mitre review concentrated on two areas during this reporting period: Impact of Coal Rank on Direct Liquefaction, and the Techno/Economic Evaluation of Slurry Phase Fischer-Tropsch Developments at Mobil Oil. The processing effects of coals ranging from lignite to eastern bituminous are being investigated for SRC-II, EDS, and H-Coal.

Preliminary results of the Mitre analysis of the Mobil two-stage slurry Fischer-Tropsch/ZSM-5 indicated an economic advantage of substituting this process for the conventional F-T reactor in a BGC-Lurgi system. For a low wax production case, coproducing SNG in addition to gasoline, the cost of gasoline may be reduced by as much as 13% over the conventional Synthoil case.

MHD PROJECTS

H.F. Chambers, Cost Account Manager

R.A. Carabetta, Chief, Coal Utilization Project Management Branch

The objective of this activity is to establish the technology base necessary to develop highly efficient, coal-fired, combined-cycle MHD/steam power plants. To meet this objective, projects are undertaken in five major categories: engineering development, support research, systems engineering, closed-cycle systems, and integrated component test activities at the Component Development and Integration Facility (CDIF) and the Coal-Fired Flow Facility (CFFF).

Closed-Cycle Systems

The goal of this project area is to develop a technology base for efficient, coal-fired, closed-cycle MHD power plants with inherent environmental and economical advantages over cur-

rently installed and operating fossil-fuel-fired electrical generation systems.

Closeout of the existing closed-cycle contract with General Electric continued. Property management disposal authority for the Valley Forge Facility was formally delegated to PETC by GSA. Removal of several hardware items from the facility has been started by PETC.

Component Development and Integration Facility

The goal of this project is to provide for the testing of 50-MW(t) power train components and systems.

During this quarter, facility modifications were continued in preparation for initiation of coal-fired combustor testing at the CDIF. By the end of the quarter, most of the major construction items had been completed, including the provision of "A" bay with a pit for the slag collection tank; the Therminol piping system in the coal preparation area; and the coal and nitrogen systems used to transport coal from the preparation area to the combustor. Repair work was begun on defective welds in the oxygen line in the "A" bay and on improvements to the cooling system for the Transrex magnet power supply.

Personnel from the CDIF also participated in a design review at AVCO for control and consolidation circuits to be installed at the CDIF.

Engineering Development

The goal of this project is to establish the technology base required for the development of major coal-fired MHD system components. The requisite data base is obtained through bench-scale and pilot-plant-scale testing of combustors, channels, magnets, air heaters, heat and seed recovery systems, and diagnostic instrumentation.

The Coal-Fired Flow Facility (CFFF) is being operated for DOE by the University of Tennessee Space Institute (UTSI) to obtain data on components in the bottoming-cycle portion of an MHD system. A low mass flow (LMF) train of components is being tested in the CFFF at nominally 8 lb/sec to obtain data on materials performance, seed recovery, pollution control, particulate characterization, and heat transfer. In its present configuration, designated LMF-3, hardware will be tested to obtain operational data on a Superheater Test Module (SHTM), Air Heater Test Module (AHTM), and Baghouse (BH).

The SHTM is designed to provide small steam superheater test sections located in three gas temperature zones with inlet temperatures of 2300°F, 1100°F and 850°F. Materials to be evaluated in the SHTM include 300 series stainless steels, Inconel, Croloy, and carbon steel.

The AHTM is designed to preheat secondary combustion air from 70°F to about 600°F while cooling the flue gas temperature from 800°F to 570°F. Its design simulates the type of heat exchanger to be used in preheating combustion air in larger systems.

Primary functions of the BH are to evaluate the use of fabric filters as a means of particulate con-

trol in an MHD system and to provide an environmental control for the LMF train. It will permit testing of a variety of fabric filter materials, air-to-cloth ratios, ease of bag cleaning, time required between cleaning cycles, and other operating parameters of a large-scale unit. The BH is designed to handle a flue gas inlet temperature of 350°F.

The LMF-3 test series will consist of eight test runs progressing from drying of the SHTM and AHTM internal refractory to a continuous 35-hour-duration coal run. Installation of the SHTM and AHTM was completed during this quarter. Delivery and installation of the BH will occur next quarter. Operations to dry the SHTM and AHTM refractory began near the end of this quarter.

Signal level and signal-to-noise level tests were successfully completed for the intrusive probe sensor under development at Mississippi State University as part of their MHD instrumentation systems program. This sensor is part of a computer-controlled probe system that will be used to position sensors in a combustion gas stream at a precise location for specific periods of time. Work also continued on testing and upgrading other diagnostic instruments, including the particle size distribution monitor, an optical NO detection device, Coherent Anti-Stokes Raman Spectroscopy (CARS) spectrometer, and a two-color laser transmissometer.

The data on nitric oxide (NO) behavior in the radiant furnace of the Coal-Fired Flow Facility at the University of Tennessee Space Institute have been analyzed by Argonne National Laboratory. These data were obtained from tests that were conducted with a slag screen installed in the primary furnace. To obtain agreement between calculated and measured NO concentrations, it was necessary to model the gas flow around the slag screen. This flow model was based on calculations using a three-dimensional thermal-hydraulics computer program, COMMIX-1A. The calculations took into account the fluid flow patterns, gas transit or residence time distributions, and the temperature and heat flux distributions in the radiant furnace.

The results of the COMMIX code were used to develop a simplified temperature/flow model for the calculation of the NO concentrations. It was assumed that the gas leaving the diffuser struck the slag screen, flowed downward partway to the furnace bottom, turned, and flowed upward through the staggered tubes, forming the lower section of the slag screen.

Kinetic analysis indicated that the NO decomposition rate is quite sensitive to the flow and temperature fields in the lower furnace. In addition, comparisons of the calculated NO concentration with the measurements indicated that the reaction mechanism and the JANAF reaction rate constants adopted by the ANL chemical kinetics code can be used for engineering calculations without modifying the constants or expanding the reaction set.

On April 30, Phase IIIC of the TRW combustor development program was completed. This program provided for fabrication and assembly of a 50-MW(t) coal-fired combustor and initiation of design verification testing. The initial base-line test results were very promising in that five of the six acceptance criteria set by DOE were met or exceeded. Slag recovery was the exception, with the 70% minimum being the criterion and 45% to 66% achieved during this early test phase that concluded March 30. More recent testing, as part of the new Phase IIID contract, has been focusing on meeting that criterion through minor modifications to the combustor and changes in the operating conditions.

At the conclusion of testing in July, the combustor and its test stand will be delivered to the Component Development and Integration Facility (CDIF). A detailed user's manual for the combustor has been written and distributed to the personnel at the CDIF. Included in the manual are blueprints for all the fabricated components, as well as assembly and operating instructions, and other information necessary for performing integrated combustor testing.

During the early testing period at the CDIF, TRW will fabricate a second-stage combustor and another first-stage unit. The combined units will undergo testing at TRW prior to shipping the second stage to the CDIF in mid-1985. The first stage will remain behind for further experimental work and also serve as a backup to the CDIF unit.

The AVCO Everett Research Laboratory performed two major activities during this quarter: continued development of the electrode finite segmentation model and an investigation of the magnetoaerothermal (MAT) phenomena. The inclusion of a finite electrode pitch in the MHD predictive model will increase calculational accuracy and, in particular, will account for the polarized cathode slag phenomena in which the cathode wall is significantly resegmented by the conductive slag layer. The model sensitivity and accuracy are presently being checked against experimental measurements.

Experiments with the Mk VI generator at maximum interaction are being continued to determine if a small channel can develop magnetoaerothermal instabilities that are predicted to occur in large channels under certain operating conditions. Evidence of such MAT effects should be seen in a transverse redistribution of electrode currents, particularly if there is a large axial current (J_x) in the channel plasma.

A series of high interaction Mk VI channel tests was conducted in the diagonal mode. Variations of the external load resulted in axial currents (J_x) of from +130 to -120 amps. No significant patterns of magnetoaerothermal phenomena were observed.

Experimental investigations of cathode wall slag shorting were continued on both the plasmatron facility and the Mk VII generator. A better understanding of this phenomena will be helpful in improving channel lifetime, particularly in the critical regions of the sidewalls adjacent to the cathodes. Here the slag polarization leads to maximum current leakage (and maximum erosion) owing to the higher electric field on the insulator walls. Particular design and material modifications have been made to the long duration channel sidewalls, which are now ready for a 100-hour test in the forthcoming quarter.

The most significant developments of this quarter in the area of MHD channel loading and control were a successful design review of the CDIF current control and consolidation circuitry that was held at AVCO with participants from PETC, CDIF, Westinghouse, General Electric, and EPRI; successful testing of new transformers and a commutation clock; and initiation of modeling and computer simulation of 16-electrode master/slave current control and consolidation.

Procurement of the CDIF hardware is proceeding according to schedule.

The Massachusetts Institute of Technology (MIT) has completed all work under contract No. DE-AC01-76ET10813, and a summary report is in preparation. An unsolicited proposal for the development and demonstration of an Internally Cooled Cabled Superconductor using niobium titanium superconductor material has been submitted by MIT. The unsolicited proposal was favorably evaluated, and a new contract with MIT for this research will be issued in the near future.

The Fluidyne final report was submitted and reviewed by PETC during this quarter. Fluidyne's primary objective was the development of a directly fired High Temperature Air Heater (HTAH)

with outlet temperatures of up to 2750°F. An additional objective was to perform limited studies of a directly fluid ceramic Intermediate Temperature Oxidant Heater (ITOH) with an outlet temperature of 1600°F.

Fluidyne concluded that ceramic materials can be defined to meet the HTAH requirements. They suggest that fusion-cast, spinel-based materials should be used in the upper portion of the cored brick matrix; and chrome-containing materials, in the lower portion. It was recommended that future HTAH work should emphasize increasing the durability of these materials. Conditions for operation of the HTAH without accumulation of seed/slag deposits have also been identified. Results of the test program indicate that HTAH valves with reasonable reliability are possible and that the control of the HTAH and its integration into the system do not present any technological barriers. Electrical isolation requirements also appear to be achievable.

Overall, Fluidyne concluded that ceramic regenerative ITOH's could be designed and built using current industrial materials and technology and that ceramic recuperative ITOH's show promise for MHD application, but that significant development work on fabrication of tubular ceramic components will be required.

Systems Engineering

The goal of this project area is to develop the engineering data base required for the design, fabrication, and operation of MHD power trains for power plants.

The objective of the Advanced Power Train (APT) Project is to develop a program plan for future MHD Advanced Power Train Development. It is being conducted in two phases: Phase 1, Plan Development; and Phase 2, Plan Implementation. Contractual efforts in this area are by two project teams: General Electric (prime contractor), AVCO, C.T. Main, and Combustion Engineering; and Westinghouse (prime contractor), TRW, Applied Energetics, and Burns and Roe.

During this quarter, both teams in the APT project conducted conceptual design studies of integrated MHD test systems that are currently being considered as potential MHD program options.

Two of the systems evaluated in this study were an 80-MW(t) plant and a 50-MW(t) plant based on siting at the CDIF. A conceptual design was also prepared for a nominal 50-MW(e) MHD system

that could be retrofitted to an existing power plant; for design purposes, the Frank E. Bird plant of the Montana Power Company was chosen. For these conceptual design studies, the contractors were directed to provide for maximum use of government-owned equipment and to utilize systems analyses previously developed in the APT program.

Results for each case included the following: (1) plant conceptual design characteristics; (2) cost estimates and construction schedules; (3) resource requirements and risk assessment; and (4) a preliminary management plan. Several characteristics are found to be common to all cases evaluated: (1) use of a two-stage, oxygen-enriched, slagging coal combustor; (2) use of a supersonic MHD generator channel together with a superconducting magnet; (3) a steam interconnection between all topping and bottoming cycles; and (4) a seed reprocessing and regenerating facility that was not fully integrated with the MHD test system. Preliminary results were presented at oral briefings on May 15 and 23, and a written report is in preparation.

The analysis by STD of the AVCO Mark VI high interaction experiments through exploratory three-dimensional simulations is continuing. Previous STD work showed that high velocity interaction is a necessary, but not sufficient, condition for observing the magnetoaerothermal current constriction on the anodes. Comparing simulations of both the AVCO and the AEDC experiments, it was found that the AVCO experiments achieved nearly twice the MHD velocity interaction parameter that the AEDC experiments did. Further simulation studies included the effects of (1) wall temperatures of 1500K and 500K compared to the original 1000K; and (2) insulating and conducting sidewalls with positive, negative, and zero Hall currents. Results, to date, show no significant anode current concentrations, although other important magnetoaerothermal effects have been seen.

Westinghouse has provided STD with a set of specifications that have led to calculated improvements in supersonic generator performance. Combining the final designs of the generators and diffusers, approximately 15% enthalpy extraction was obtained for both the supersonic and subsonic designs. However, the diffuser performance itself is typically 10% to 15% higher for the supersonic as compared to the subsonic designs. A graphical display of the completed designs is now being prepared.

Supporting Research

The goal of this project area is to provide fundamental supporting research for application to advanced MHD hardware development.

Work at the Stanford University high-temperature gas dynamics laboratory progressed in the following areas:

- Boundary layers and generator loss mechanisms: Direct measurements of secondary flows in an MHD channel have been made for the first time and indicate the importance of such flows.

- Plasma nonuniformities and instabilities: Measurements of the propagation of magneto-acoustic waves in an MHD channel have been made, and they correlate well with theoretical predictions.

- Seed-slag interaction: A survey of the available thermochemical data has been completed and reveals significant discrepancies. A computer code is being developed to model seed-slag interaction in an MHD generator.

- Disk generators: A computer model has been developed to predict electrical breakdown in disk generators. The results compare favorably with earlier measurements.

- Temperature diagnostics: A diagnostic test section has been completed, and work has begun on testing a fiber-optic pyrometer in an ash-laden combustion flow.

The scope of work at Multi-Tech includes environmental research, facility monitoring, and development of the environmental portion of an MHD data base.

Multi-Tech is operating three air quality monitoring stations at the CDIF in order to develop an updated air quality base line in preparation for future coal-fired MHD combustion testing. Although previous air quality data had been obtained for the Butte, Montana, area, a new base line will be required because curtailed local open-pit copper mining has resulted in a 20% to 50% reduction in airborne particulates in the first half of 1984.

An annual quality assurance audit was conducted by Multi-Tech personnel of the environmental-monitoring stations at the CFFF.

Data on effluents from MHD facilities and predictive models for physical and chemical properties of effluents in an MHD system are being

organized by Multi-Tech for the PETC MHD data base.

Research at MERDI is focused on the development of a long-duration electrode concept, consisting of a molten metal electrical conductor contained in a ceramic insulating material. Research efforts continue on the development of a ceramic fabrication technique that may be used to construct a model electrode for testing.

Pacific Northwest Laboratory is conducting ongoing research to select materials for ceramic electrodes for advanced MHD channels.

The development of the current lead-out materials has focused on the properties of In_2O_3 - SnO_2 compositions. Three crystallographic phases have been identified in the compositions: (1) a tetragonal phase containing mostly SnO_2 , (2) a rhombohedral phase containing $\text{In}_4\text{Sn}_3\text{O}_{12}$, and (3) a body-centered cubic phase containing mostly In_2O_3 . The corrosion resistance of the phases are rated as tetragonal > rhombohedral > body-centered cubic. The electrical conductivity is rated as body-centered cubic > rhombohedral > tetragonal. Consequently, the rhombohedral phase is the best compromise for corrosion resistance and electrical conductivity.

The examination of insulator materials has focused on two areas: (1) the molten salt corrosion of magnesium-aluminum spinel and (2) the obtaining of quality powders of aluminum nitride (AlN). The spinel appears to degrade by interactions of molten salt with the grain boundaries when the insulator is located at the cathode but not when the insulator is located at the anode. Aluminum nitride may be a very good MHD channel insulator for those channel designs that keep the insulator at temperatures less than 1200K. The AlN has a high thermal conductivity (greater than boron nitride and silicon nitride), good high-temperature thermal stability, and high electrical resistivity. Samples of the powders will be obtained, fabricated into test compacts, and laboratory-tested to determine their compatibility with coal slag and molten salts and to better define the limits of their thermal and electrical stability.

Westinghouse Electric Corporation has concluded the work performed in their test facility and has submitted a draft of the Final Report for PETC review. This MHD Generator Electrode Development Program was directed towards the development of economic MHD electrodes, with emphasis on alternatives to platinum, and of insulator designs that will sustain long-term open-cycle, coal-fired MHD generator operation.

Laboratory arc erosion, electrochemical corrosion, and engineering tests under simulated MHD operating conditions were conducted on both hot-wall electrode materials as well as cold-wall candidate materials. The relative ranking of can-

didate materials in order of most favorable lifetime were chromium, Ebrite 26-1, Inconel 601, and 330 Stainless steel. The engineering test rig included a 0.5-MW(t) combustor, 3 Tesla Magnets, and a 12.5 cm² flow cross-section channel.

ALTERNATIVE FUELS TECHNOLOGY

R.C. Kurtzrock, Cost Account Manager

R.A. Carabetta, Chief, Coal Utilization Project Management Branch

The goal of these projects is to establish the feasibility and acceptability of using coal-based mixtures as alternate fuels for utility and industrial applications.

Combustion and Fuel Characterization of Coal-Water Mixtures (CWM) — Combustion Engineering, Inc.

Vendor "A" determined that they could not make CWM from Black Creek coal to meet the specifications set by the CWM Combustion and Fuel Characterization program; coal loading would be below minimum limit. They also determined that on-spec slurry could be made from Upper Freeport coal. Vendor "A" also determined, from a 400-lb sample of Cedar Grove coal, that CWM can be manufactured to exhibit desired slurry properties. Cedar Grove coal is the last coal selected for this project.

The preliminary testing phase of Gulf Research and Development Company's erosion test loop was completed. Results indicate a consistently increasing erosion rate with increasing velocity. Loop-flow velocities of 6 to 8.5 fps (shear rates of 600/sec to 800/sec) produced erosion rates of 53 to 230 mils/year, respectively. While the velocity could not be reproduced exactly, all test results were consistent, yielding a well-defined relation between velocity and erosion rate.

Additional erosion loop tests were performed using a fresh CWM made from a 5.7% ash, Splash Dam coal and prepared by Vendor "C". The tests were conducted at shear rates of 900, 1000, and 1100/sec. Erosion values were 79, 88, and 103 mils/yr, respectively. These values are very similar to those found when testing the first CWM made from coal of unknown ash content and prepared by Vendor "C" (not a candidate for inspection in this study).

Lack of firm response and/or product delivery by two candidate burner vendors has resulted in involvement by DOE to clarify the vendors' status and participation in the project.

Initial firing of the second batch of reference slurry indicates a higher fuel-side pressure drop than what was previously obtained with the fuel used during pre-matrix testing. After considerable investigation, it was determined that the fuel needed to be subjected to a high-shear environment prior to firing. This served to lower the fuel's apparent viscosity to a point where lower fuel-side pressure drops were obtainable. Atomization testing conducted on the second batch of fuel indicated essentially identical pressure drops and atomizer performance after the CWM was subjected to the high-shear handling system of the Atomizer Test Facility (ATF). Our current plan is to utilize the second batch of CWM for testing by subjecting it to a high-shear regime prior to the test runs.

Testing of CWM No. 5 was completed in the Fireside Performance Test Facility (FPTF). The test fuel was prepared by Slurry Vendor "A" from Splash Dam coal beneficiated to 5.7% ash. This CWM had a solids loading of 69.5% and exhibited good static stability. Some problems were encountered during cold-flow atomization tests when the slurry was exposed to extended high-shear mixing. Vendor adjustments were made to the CWM. Results of the ATF tests indicate relatively high energy requirements were needed for the test-fuel atomization. Preliminary results from the FPTF performance testing indicated the test fuel had ash slagging and fouling characteristics similar to previously tested Splash Dam CWM's. Testing was conducted at the high-firing rate with peak furnace temperatures of 3000°F to 3100°F and convection section temperatures up to 2350°F. Combustion was very stable throughout testing. Ash deposition on both radiant and convective heat-transfer surfaces was low.

Fireside performance testing of CWM No. 8 is under way. The test fuel was prepared by Slurry Vendor "A" from Upper Freeport coal beneficiated to approximately 11% ash. This CWM had a solids loading of approximately 70%, with a

viscosity of approximately 2300 cp at 100 sec⁻¹, and a power law index of 0.9. The storage/agitation and shear history of the CWM required particular consideration in order to allow satisfactory testing. Preliminary results of ATF atomizer spray characterization indicated the CWM was difficult to atomize. The marginal fuel properties of this CWM are apparently attributed to poor slurring characteristics of the high-ash feed coal.

Performance testing is being conducted on CWM No. 8 at two different thermal loadings. The first run (80 hr) performed at the intermediate firing rate has been completed. Peak furnace temperatures during these tests were controlled from 2800°F to 2900°F. Ash slagging characteristics were low-to-moderate, as friable, sintered water-wall deposits were generated, which were readily cleanable with soot blowers. Ash fouling characteristics were also low-to-moderate, as convection probe deposits accumulated at a moderate rate. However, deposits were easily cleanable at gas temperatures up to 2300°F. The thermal loading will be increased for the next test run.

While the combustion results of the pretest shakedown of the Combustion Engineering (CE) wall-fired burner were very good, CE elected to utilize their discretionary opportunity to modify the burner before further testing. These modifications were aimed at reducing burner pressure drop. Combustion matrix testing of the "high-swirl/wall-fired burner" is being conducted in the Sub-Scale Burner Facility. Approximately 50% of the combustion matrix has been completed. Initial observations indicate good flame stability. Modifications to the burner, performed after the initial evaluation, were successful in reducing burner air pressure drop.

The Keeler atomizer has still not been delivered to CE. Keeler plans to run a second series of tests using the Atomizer Test Facility (ATF) to determine whether their problems are fuel related.

The atomizer from the refractory chamber burner was subjected to the initial evaluation in the ATF using reference slurry. This atomizer met the performance criteria developed for atomizers in this program. Based on this testing, this atomizer will be used for the combustion test of the refractory burner.

Plant Equipment Selection and Performance Using Coal-Water Mixtures — TRW, Inc.

A program was installed to acquire, store, retrieve, average, and display data to allow equip-

ment check-out and instrument calibration with water to proceed. A second computer program was written to expand the system function to include alarm, dynamic limit adjustment, storage, retrieval, display of data, and control. This program exceeded the system display of data and flow control, and required software overlay. TRW has opted to procure and install controllers, and reduce the alarm/control requirements for the IBM/PC/DAS-510 system.

The reduced-requirements software has been installed and is supporting shakedown. The test plan has been revised for the new mode of operation. The controllers, which will allow for unattended operation of the test loop, are on order.

Three 1500-gallon tanks of CWM have been received for shakedown and screening in the TRW test loop. The generic (shakedown) slurry from Vendor "A" is 3.6% ash that upon arrival had solids contents, as a function of tank depth, from 67.1% to 74.8%. The CWM had been transported through freezing weather. After sparging with nitrogen, the mixture was homogeneously 68.5% solids. Slurry No. 1 from Vendor "C" is high-ash Splash Dam CWM that was 71% solids upon arrival, and homogeneous, as a function of tank depth. Slurry No. 2 from Vendor "A" is also high-ash Splash Dam CWM. Upon arrival, solids content varied slightly, as a function of the tank depth, from 70.1% to 69.7% to 70.4% solids. A 1 1/2-inch layer of material termed "peanut butter" was on the shipping-tank bottom.

A generic slurry was used to test the operation of the facility, the computer system, operating instructions, and sampling procedures. The CWM was transferred from the day tank to the run tank using the lobe pump. Test matrix "A" was begun, using the twin-screw pump to establish variable-shear operation (attended), followed by unattended controller-controller, constant-shear operation at an overnight rate of 30 gpm. The system automatically shut down because of a day tank low-level alarm. The system was restarted without incident. The CWMs had remained pumpable even in the noncirculating lines. After another four hours of operation (10 cumulative hours of operation), the system was shut down and flushed with water for the weekend shutdown.

A new charge of generic slurry was loaded into the day tank. This run was to test high-temperature operation and also operation at high back pressure (partially closing burner nozzle simulation valves) at the end of the forty-four hour run. The CWM was heated to 104°F and left overnight

in the day tank with the tank mixer running. Additional slurry was added to the system and heated. Operation of test matrix "B" was then begun. Variable and constant shear operation was performed throughout the afternoon. The first all-night, unattended operation was achieved.

Development of a Vortex Containment Combustor for Coal Combustion Systems — Energy and Environmental Research Corporation

A series of isothermal experiments was performed to study the influence of exhaust duct modifications on the Vortex Containment Combustor (VCC) system performance. The modifications included the addition of a conical expansion to diffuse the swirling exhaust flow and of a nozzle exhaust lip to prevent flow separation as the combustion gases leave the VCC. These modifications proved more effective as the exhaust diameter became smaller. At an exhaust diameter of 4 1/2 inches, pressure drop decreased by 25%, with a reduction in retention efficiency of only 1% using these modifications. This approach, at an exhaust diameter of 5 3/4 inches, caused the same reduction in pressure drop but lowered the retention efficiency by approximately 5%.

Upon conclusion of the exhaust modification testing, the detailed design drawings for the prototype VCC were finalized and submitted to the Energy and Environmental Research Corporation fabrication crew for construction.

Construction of the prototype Vortex Containment Combustor (VCC) is proceeding as planned. The active zone of the combustor measures 28 inches in diameter at a depth of 7 inches. The slag collection zone has the shape of a truncated cone, 12-inches long, 12 inches in diameter at the open end (which attaches to the active zone), and 6 inches in diameter at the closed end. The internal volume totals 3 cubic feet. The exhaust has been chosen initially to be 7 inches in diameter. Air is injected through twelve slots that encircle the active zone. The slots are 7-inches high, 1/2-inch wide, and positioned to inject combustion air at 45° from the tangent. Fuel will be injected through four water-cooled tube injectors with 1.12-inch internal diameters. A multilayer refractory design is used to minimize heat loss. Only a high density, 95% alumina refractory will be exposed to flame contact. A 1-inch-wide slag trough, running the length of the slag cone, will slice through the refractory to allow slag drainage. The trough will be back-heated by two spiral bayonet, silicon carbide heating elements to ensure fluidity of the rejected slag. A 1/2-inch-dia-

meter hole will pierce the refractory and will be used to sight an ultraviolet flame detection safety device. Four type K and four type S thermocouples will be used to monitor the refractory temperature. The prototype VCC is designed in a modular fashion to facilitate disassembly for observations, alterations, or repair.

Integrated Superfine Coal Combustion System for Converting Oil-Fired Steam Generators to Coal Firing — Foster Wheeler Development Corporation

Superfine Coal Combustion System performance and operating parameters were selected and modified to reflect suggestions made by Dr. R. Hise, of Consolidated Natural Gas, during the project review meeting at PETC. The modifications were as follows: (1) Increase slurry concentration to 30% coal by weight to reduce pumping-energy requirements and (2) increase slurry concentration to 75% coal by weight after separation in the hydrocyclone to reduce blowdown and stack moisture losses.

These changes helped reduce the amount of energy required by the slurry heater from 20 MW(t) to 12 MW(t) (67 to 41 x 10⁶ Btu/hr). A trade-off was made to determine the sensitivity of the process to the final supercritical temperature before expansion. The results indicate that by reducing this temperature by 50°F, the energy requirements will decrease by 1.7 x 10⁶ Btu/hr.

The performance and operating parameters were further revised as a result of recent work and new information from vendors on performance data of auxiliary equipment, such as slurry pumps, cyclones, and hydrocyclones. Data from vendors have been difficult to obtain because of the "first-of-a-kind" nature of the process.

The system's mass and energy balances are being updated and improved as new information develops, such as component pressure drops and thermal losses.

Work continues on the computer program that will size the supercritical slurry components. The heat transfer and pressure drop subroutines of the program are being modified to account for the coal portion of the slurry. Modifications to the finite-element program employed for heat-transfer/sizing calculations were completed. The program can now perform calculations for the recuperator (slurry-to-slurry) and for the slurry (steam-to-slurry) heat exchangers. Work continues in the pressure drop subroutine to include the effects of the slurry.

The program divides the heat exchanger into elements; the outlet conditions from the previous element are used as the inlet conditions for the next element. Because of the large changes in specific heat of the supercritical water near the supercritical point, it was necessary to limit the length of the control element to 1 ft. Different results were obtained with control elements of 10 ft to 1 ft; no significant differences were found using smaller elements.

Preliminary sizing runs were made for the recuperator. The shell o.d. was limited to 3 ft because of manufacturing constraints [the high slurry pressure (5000 psia) requires very thick shells]. The length of the vessels was limited to 100 ft because of transportation constraints.

Computer runs indicate that the recuperator surface/length requirements are too large (more than 200 ft) for the condition selected (781°F slurry leaving the recuperator). A trade-off study will be made during the next reporting period between the slurry outlet temperature and the area requirements.

*Development of Pulsed Coal Combustor
Fired with CWM — Management and Technical
Consultants, Inc.*

The results of the prior-art survey on pulse combustion were reported to PETC. The results of the definition of potential applications and specifications of performance and operating parameters are in the process of being assembled into reportable format.

The primary emphasis of the prior-art survey was placed on the technical literature, i.e., technical reports, journal articles, and conference proceedings. The patent literature was also included in the survey but, because of late arrival of many of the patents, will be reported on in a Task 2 report supplement to be submitted later. A preliminary screening of the technical literature identified sixty-nine references containing information of potential usefulness to CWM combustor design. A task report submitted to PETC conveys key data and conceptual design information contained in the references, and serves as a guide to the significant technical content of each reference. The report concludes with a bibliography that categorizes the references according to type of study and type of fuel.

Data on pulse combustion are being reviewed. Strong and weak areas in the literature data base are being identified according to type of data

(combustion, heat transfer, etc.) and type of combustor design.

The DOE and Gas Research Institute (GRI) support programs in the area of pulse combustion are of particular interest to the current study, as they have generated technical data and fundamental insights useful for design of a CWM combustor. Under the DOE program, a gas-fired pulse combustor was built and brought into operation at Argonne National Laboratory (ANL). Design criteria and operational experience gained in that program are valuable input to the present program. Using that unit, useful heat-transfer data were obtained, and correlations were developed relating heat transfer to axial position and operational variables. The GRI program has involved construction and operation of test units at Battelle-Columbus Laboratory and the American Gas Association laboratory, as well as tests on the ANL unit. A large amount of practical information has been obtained relating combustion characteristics, acoustics, and heat transfer to such factors as valve design, combustion chamber and tube configuration, and firing rate. The GRI program has also been supported by heat-transfer investigations on a test unit at Purdue University. Substantial theoretical understanding of the process has been generated by the DOE and GRI programs.

The most substantial pulse-combustion development programs aimed at coal and heavy-oil fuels have occurred in Germany and the USSR over the past three decades. Both programs have been brought to full-scale demonstration stages in which pulse-combustion burners have been retrofitted to boilers. Meanwhile, several independent programs involving pulse combustion of coal have occurred in the U.S., including a commercial development effort by a private company, a lignite burner developed by the U.S. Bureau of Mines, and a recent DOE program to explore application of pulse combustion to stoker-fired boilers.

Pulse-combustion development programs on clean fuels, as well as those on heavy oils and coal, have been primarily empirical in nature. Little use of theoretical calculations or semi-empirical correlations has been employed in development of the combustor designs. However, one of the goals of the DOE and GRI support programs is to develop correlation and theoretical insights to improve the understanding and predictability of the phenomenon. Also, a number of theoretical and correlation studies of pulse combustors have been conducted independently at various research institutions. A major objective of

the present study is to bring this information together to formulate a modeling basis for guidance of the CWM combustor design. The technical literature contained significant theoretical analyses and correlations in three areas of importance to modeling of a CWM-fired pulse combustor: (1) theoretical analyses and models of fuel-particle combustion in a pulsating field; (2) theoretical analyses and correlations to predict the effect of flow pulsations on convective heat transfer; and (3) model elements capable of predicting pulsation frequency and amplitude versus design variables.

Selection of pulsed-combustor applications was based on population characteristics, and design and operating requirements of generic types of boilers and process heaters in the U.S. Preliminary steam configurations have been developed for a number of feasible applications. A report showing the preliminary configurations is being prepared.

Ranking criteria for Systems Analysis/Concept Evaluation have been established, and potential candidate systems have been selected. Candidate systems are being screened to select those to receive design analysis. Two systems have now been selected. Fuel characteristics, performance goals, and operating requirements have been identified for the systems selected.

Work was initiated on basic hardware and facility planning that is independent of the specific combustor design. This task was assigned to KVB, in whose laboratory the tasks will be performed.

Models available in the literature have been reviewed and assessed. Useful model elements have been extracted. Work was begun on development of a computer code to reflect usable model elements already available, and useful theoretical relationships otherwise available in the literature.

*Feasibility Evaluation of Wet Oxidation
for Combustion of Coal Slurries —
Science Applications, Inc.*

Wet oxidation data assessment activities were completed, and data are being used in systems conceptual analysis.

The conceptual design analysis will also include considerations of bench-scale and pilot-scale efforts.

Performance and operating parameters for bench-scale studies have been investigated. The process flow sheet for the bench-scale system

has been updated. Discussions have been held with potential suppliers of the equipment.

The base-line case for pulverized coal firing has been selected for comparison with the wet oxidation process. Cost analysis will be consistent with the EPRI Technical Assessment Guide, and will be escalated and scaled in accordance with those guidelines. The capital costs will be compared with those reported in EPRI PE-1865.

Costing data-base information for the conceptual design analysis was obtained from the American Association of Cost Engineers. Additional cost and conceptual references were also obtained and reviewed. The plant sections have been defined to assure comparability with existing information.

The effort has been focused on the identification of equipment for both commercial-scale and bench-scale systems. Coal type and properties, equipment capacities, and primary system configurations and comparison systems were discussed with the PETC Technical Project Officer.

Preliminary recommendations for additional work were assembled and submitted to PETC for review and comment. The need for bench-scale data for reactor scale-up was discussed extensively.

Additional attention has been focused on the bench-scale system earlier in the project than originally planned. This activity will be accomplished in parallel with the conceptual design studies.

*Feasibility of a Hot, Dry-Ash Impact Separator —
Solar Turbines, Inc.*

Ceramic separator components for preliminary tests have been received. Each item was fabricated by Babcock and Wilcox Company from a high-alumina, vacuum-cast refractory (Cerox 700) in quantities of five. Two impactor orifice sizes are available for testing (1-inch diameter and 1/2-inch diameter).

The test module case and associated hardware have been fabricated. Assembly and installation have been started.

Coals to be used in dry ash and slagging tests are now on hand. An Illinois coal and a Wyoming coal are available for slagging tests, and a Colorado bituminous coal is available for low-temperature tests.

An Illinois coal was received from Energy and Environmental Research Corporation for use in

the impact separator in pilot-scale tests. The coal has a 3.9% to 4.0% sulfur content and an oxidizing ash-fusion temperature of 2324°F. A variance will be obtained to allow use of this coal, since local limits are 0.5% sulfur by dry weight.

An investigation of potential inaccuracies in particle measurements, owing to condensation of fumes in the sample probe, shows that some size-distribution shift may occur at high-temperature operation, since the amount of volatile compounds increases with combustion temperature. More rapid quenching of the gas stream in the sample line may cause a slight shift in particle distribution to smaller size due to nucleation rate effects. Nucleation rate effects, however, have a greater influence on submicron particle-size distribution. The particle-size range (2 to 5 microns) important to this study is not as susceptible to these effects. The effects can also be minimized by providing identical conditions for upstream and downstream sampling. A percent reduction of concentration in each particle-size category will provide an accurate measure of performance of the impact separator device, even though absolute size distribution of the stream may include some small error.

Advanced Slagging Coal Combustion System — TRW, Inc.

The combustion system refurbishments for full (10MM Btu/hr combustor) system characterization testing were completed during the reporting period. Initial check-out testing was completed with the coal-fired precombustor.

The test facility modifications necessary to support check-out firing of the 50MM Btu/hr combustor were initiated and accelerated to allow preliminary cold-flow characterization and functional check-outs.

First-stage testing on the 50MM Btu/hr combustor was completed on TRW Product Development funds. The tests revealed that performance levels would meet or exceed those obtained from testing with the 10MM Btu/hr combustor. The data are currently being analyzed and will be made available to DOE for inspection. The data support will also include a checklist of requirements and conformance to the Statement of Work. This document will verify operational capability and hardware integrity for use on the DOE project.

An interface meeting between Stone & Webster Engineering Corporation (SWEC), Foster Wheeler Boiler Corporation, and TRW was held at SWEC headquarters in New York. Surveys of the generic

classes of retrofit types revealed that there are four representative retrofit cases that are viable for coal conversion. A summary of these cases is presented in Table 5.

There are two differences between the selected case studies and those in the original work statement. The process heater case has been changed to a single-combustor, industrial-package boiler. The package-boiler case is a more representative retrofit for replacing oil with coal. The conversion economics will be similar to those of a process heater except that the combustion product quality will be more stringent. The second difference is the elimination of the 85MM Btu/hr combustor size. This combustor size has a limited application judging from the number, age, and type of utility boilers amenable for retrofits.

The selected retrofit cases to be studied cover the entire range of anticipated applications. The least stringent requirements correspond to the kiln. The retrofit fuel is tentatively indicated to be CWM, should a single retrofit be made. Multiple retrofits at the same site may favor pulverized coal over CWM. Stone Webster Engineering Corporation will determine the economic sensitivity for the conversion fuel, i.e., the number of units to be retrofitted to allow pulverized coal to have an economic advantage over CWM.

The industrial-package boiler retrofit with CWM for No. 2 and No. 6 oil represents a very large segment of small units currently in the field. Experience with the TRW Cleveland retrofit will assist this study. The selection of CWM as the retrofit fuel was made on the basis that most of the application sites would not have the room for coal-handling facilities nor would the economics favor pulverized coal.

The large industrial boiler (300,000 lb/hr steam) represents the more stringent requirements with multiple-combustor retrofits. The fuel selection will be chosen ultimately from an economic comparison.

The most stringent requirements are those associated with the conversion of a gas-fired utility boiler. The size (150MM Btu/hr) and number (24 to 26) of combustors are compatible with a broad range of 400-MW(e) units.

A CE Corner-Fired Unit has been tentatively selected as the utility boiler retrofit case for the project. This selection was based on the market segment percentage of CE corner-fired units that could be retrofitted (@ 58%) in the nominal 400-MW range. The subcontractor, SWEC, is working with a southern utility to determine if enough

Table 5.
Retrofit Cases to be Studied

Type Unit	Original Fuel	New Fuel	Unit Rating lb/hr Steam or MW _(e)	TRW Combustor Size MM Btu/hr	Approx. No. Combustors	Mfg.
Kiln	Gas or oil	CWM ¹	— —	20	1	TBD ²
Industrial Package Boiler (D-Type)	No. 2 or No. 6 Oil	CWM	40,000 lb/hr 150 psig sat.	50	1	FWBC
Industrial Field Erected Boiler	No. 2 or No. 6 Oil	CWM or PC	300,000 lb/hr with some superheat	50	8	FWBC
Utility Boiler	Gas	PC	400 MW _(e) with superheat	150	24 - 26	TBD

¹SWEC to determine economic viability.

²To be determined.

information about the boiler can be obtained or if CE must be contacted directly. A go, no-go decision on the CE boiler selection will be made during the next reporting interval depending upon the amount of information that can be obtained. Alternate choices are available, such as the more conventional wall-fired units manufactured by B&W and Foster-Wheeler.

Stone Webster Engineering Corporation has contacted several kiln manufactures to determine if the kiln size of 20MM Btu/hr is representative. Apparently, this size represents only a small segment of kiln applications, while representative sizes begin around 50MM Btu/hr. The kiln survey study is continuing in order to select a size for which a reasonable retrofit case may be studied.

FLUE GAS CLEANUP

J.E. Williams, Cost Account Manager

F.R. Brown, Chief, Environmental Control Technology Project Management Branch

The purpose of the Flue Gas Cleanup Program is to develop a technology base for low-cost post-combustion control of undesirable pollutants produced during the combustion of coal. The program is directed at combined flue gas cleanup in which SO₂, NO_x, and particulates are captured simultaneously, eliminating the need for costly sequential processes for individual pollutant removal.

Electron Beam/Lime Spray Dryer Combined NO_x/SO_x

The objective of this project is the pilot-scale evaluation of SO₂ and NO_x removal from flue gas by means of a lime slurry spray dryer followed by electron beam treatment. The effect of the high-energy electrons is to excite the flue gas molecules, producing an abundant and reactive supply of radicals, ions, free atoms, and secondary electrons. Those species containing oxygen atoms can oxidize the SO₂ and nitrogen oxides in the flue gas to higher oxidation states such as acids, which then readily react with the excess lime carried over from the spray dryer or with the alkaline fly ash.

The pilot-scale system draws a slipstream from a 150-MW coal-fired boiler at the TVA Shawnee Steam Plant in Paducah, Ky. The system includes a spray dryer, an electron beam treatment chamber, and a fabric filter. The E-Beam is placed between the spray dryer and the fabric filter, and in this way, the electron beam effectiveness benefits from the low-temperature, high-humidity conditions at the spray dryer exit. In a similar fashion, the electron beam process enhances the economy of the spray dryer. Since the E-Beam process removes SO₂, the spray dryer is not required to provide high SO₂ removal efficiency, and good lime utilization is realized.

The system has been installed, shakedown tests were completed, and the test program was begun. However, testing has been suspended since April 16, 1984, pending completion of negotiation of a contract modification to extend the time and add additional funds to complete the testing, and for approval of the subcontract between Research-Cottrell and TVA. Testing is expected to be resumed early next quarter. (Cottrell Environmental Sciences)

Electron Beam/Ammonia Injection Combined NO_x/SO_x

The primary objective of this project is to demonstrate the feasibility of the Electron-Beam Process for removing SO_x and NO_x particulates from coal-fired flue gases. This demonstration unit will have a capacity of 15,000 to 20,000 scfm and a testing period of more than 12 months. Numerous parametric tests will be conducted during a six-month period, and a long duration test of an additional six months is planned during final testing. Another objective of the PDU Program will be to analyze the by-product powder and its potential utilization as an agricultural fertilizer. Previous investigations have indicated that the by-product contains the same fertilizing capabilities as commercial ammonium sulfate/nitrate. The demonstration site is the E.W. Stout Plant No. 6 boiler of the Indianapolis Power & Light Company located in Indianapolis, Ind. The project is being managed, constructed, and tested by Ebara International Corporation with participation in the project by the Indiana Energy Development Board, Indiana Electric Association Member Companies, Amax Coal Company, C.F. Industries, and Ebara Corporation, and with the U.S. Department of Energy participating under a Cost-Sharing Agreement.

Bechtel Group, Inc., of Ann Arbor, Mich., was selected in late May for the on-site construction. Construction should be completed and testing is scheduled to begin in November 1984. (Ebara International Corporation)

NOXSO Combined NO_x/SO_x Process Evaluation

The objectives for this project are (1) to study the process chemistry and factors that influence the chemistry, (2) to identify a set of operating conditions that will provide for the efficient removal of SO₂ and NO_x, (3) to obtain kinetic data for use in designing large-scale systems, and (4) to develop the design for a full-scale NOXSO system and estimate the unit capital and operating cost for the system. A test program was designed to achieve these project goals.

The process utilizes sodium on a alumina substrate material operating at approximately 120°C in a fluidized-bed reactor to remove over 90% of both the SO₂ and NO_x. The spent sorbent is regenerated at approximately 550°C to produce elemental sulfur. The NO_x is converted to gaseous N₂.

The process is being tested on a small bench-scale slipstream test unit at TVA's Shawnee Power Plant, near Paducah, Ky. Although the process is similar to the old alkalized alumina process tested earlier in-house at PETC, there are significant differences, including a lower operating temperature. Sorbent attrition in tests to date has not been a problem, as it was during the testing of alkalized alumina. However, it is important that the sodium level (wt%) be controlled below a critical level that is probably between 6% and 7%. The substrate material supplied by The Davison Division of W.R. Grace has proved to be very sturdy material. Target goals of 90% removal of both SO₂ and NO_x have easily been attained during these small-scale tests.

For the immediate future, NOXSO will continue to conduct the ongoing research program through this calendar year. This work will be directed toward obtaining a better fundamental knowledge of the chemical mechanisms and process-operating variables.

A cooperative agreement with the U.S. Department of Energy in-house at PETC is being considered that would utilize the fluid-bed system and associated equipment and instrumentation previously used for development of the fluid-bed copper oxide process for larger size (about 1 MW) testing of the NOXSO process. These tests are targeted to begin in FY85. (NOXSO Corporation)

Glow Discharge Combined NO_x/SO_x Process Evaluation

The objective of this new project is to evaluate and assess the potential of this novel new concept for simultaneously controlling 90% of both NO_x and SO₂ from coal-fired boilers. The process uses a glow discharge to initiate reactions similar to those that occur in the electron-beam-type processes. The process is projected to use less power than the E-Beam processes and should not require radiation protection, as do the E-Beam processes. It may even be feasible to use existing ducts or expanded sections of ducts for installation of this process, which could lead to a simple, inexpensive, easily retrofitted type of process. Equipment for the small bench-scale tests is currently being acquired and assembled. Testing is scheduled to begin during the next quarter. (Westinghouse Research and Development Center)

Moving-Bed Copper Oxide Combined NO_x/SO_x Process Evaluation

The Energy Systems Group of Rockwell International has recently begun a 24-month program to test and evaluate a single-stage process for simultaneously removing 90% of the NO_x, 90% of the SO_x, and 99.9% of the particulates from flue gas. The process uses a novel contactor-filter with a moving bed of copper oxide absorber-catalyst. At 400°C, NO_x is catalytically reduced to N₂ by adding NH₃ to the flue gas, and SO_x is absorbed by the copper oxide. The same contactor/filter also removes the particulates from the flue gas. The absorber-catalyst is regenerated by reacting the copper sulfate formed with a reducing gas such as hydrogen or methane, and is then reused in the process.

The program consists of three phases. Phase I involves the design, modification, and operation of an existing contactor-filter test unit to determine the performance and to identify important operating parameters for the process. The tests will be run on simulated flue gas containing SO₂, NO_x, and fly ash at levels representative of flue gas from coal-fired boilers. During this phase of the program, an open loop will be used in which the spent absorbent will be regenerated and recycled to the contactor in batches. In Phase II, the critical features of the overall process will be evaluated while operating in a continuous integrated closed-loop mode on the simulated typical flue gas. In Phase III, the evaluation of the technical feasibility of the overall process, and the development of an initial projection of process economics will be carried out. Catalyst selection for

Phase I is nearing completion, and the design and modification of the moving-bed contactor-filter is currently in progress. Testing is scheduled to begin during the next quarter. (Rockwell International Corporation)

Sulf-X Combined NO_x/SO_x Process Evaluation

The objective of this new project is to evaluate the capability of the Sulf-X Process to remove at least 90% of the SO₂ and NO_x from coal-fired combustion gases. Important operating variables identified and the data acquired will permit a conceptual design for a 500-MWe system to be developed for use in assessing the technical and economic feasibility of the process. The integrated testing program is aimed at determining optimum operating conditions. Impact of key operating variables on SO₂ and NO_x removal efficiency will be assessed, and calciner operation typical of a commercial-scale Sulf-X Process will be model-tested. Alternative reductants, such as petroleum coke, metallurgical coke, and bituminous coal, will be tested. Waste discharge rates will be monitored and characterized. A 30-day continuous test of reliability run at optimum conditions will be conducted.

The Sulf-X FGD process is a wet regenerative process developed in 1974 by Dr. H.C. Bramer and Edward Shapiro. Successful pilot tests were conducted during 1977 at a 1.0-MW coal-fired boiler facility at Fort Benjamin Harrison and subsequently at another 1.0-MW unit in cooperation with Westinghouse Electric Corporation's Advanced Energy Systems Division. The tests were funded by DOE. The present facility located at the heating plant of the Western Center Hospital, Canonsburg, Pa., is about 1.5-MW capacity and was completed in 1982. It has operated almost continuously since early 1983 removing SO₂ and NO_x from the flue gases of one of the three stoker-fired heating plant boilers.

Under the current contract, the test facility in Canonsburg, Pa., will be modified to add a second-stage reactor to obtain improved NO_x removal capability. Modification of the test facility is now under way, and testing is scheduled to begin during the next quarter. (NUS Corporation)

Combined NO_x/SO_x Removal with ZnO in a Spray Dryer - Bench-Scale Tests

The objective of this project is to demonstrate and evaluate the technical and economic feasibility of a process employing ZnO in a spray dryer, and a fabric filter to remove at least 90% of the

SO₂ and 90% of the NO_x from coal-fired combustion gases. A bench-scale test program is being directed toward determining reaction mechanisms, evaluating performance, identifying important operating variables, and producing data required for conceptual design of an optimized pilot plant if the process appears promising. The conceptual design and data will be used to assess the technical and economic feasibility of the process. The test equipment has been acquired and assembled, and testing was recently begun. Testing will be continued in the next quarter. Results to date are too preliminary to be meaningful at this time. (Battelle Columbus Laboratories)

Combined NO_x/SO_x Removal Process with Metal-Exchanged Zeolites - Bench-Scale Tests

The objective of this new project is to evaluate the potential for using metal-exchanged synthetic zeolite to simultaneously catalyze the selective destruction of nitrogen oxides using ammonia as the reducing gas and chemisorb SO₂ in flue gases from coal-fired power-generating plants. The evaluation program comprises three phases: (1) laboratory catalyst development, (2) bench-scale testing, and (3) an economic evaluation of the process based on the results of the developmental work. A synthetic mordenite zeolite was selected as the support material because of its known high catalytic activity for prompting the selective destruction of NO_x, and its high surface area for chemisorbing SO₂. An automated test system for performing NO_x destruction - SO₂ adsorption and adsorbent regeneration studies has essentially been completed and is presently undergoing check-out tests. This test apparatus will be used to obtain the needed NO_x conversion, SO₂ adsorption, and adsorbent regeneration data, including long-term testing, to perform the economic evaluation for the proposed process. (Science Applications, Inc.)

Study of Acoustic Agglomeration of Power Plant Fly Ash

Acoustic agglomeration is an intermediate treatment of aerosols containing submicron-sized particulates. The acoustic-agglomeration treatment then will result in the formation of substantially larger particles in the form of agglomerates, which can then be removed more efficiently by conventional particle-removal devices, such as baghouses, electrostatic precipitators, scrubbers, and cyclones. In acoustic agglomeration, the aerosol is subjected to high-intensity sound in the

vicinity of 160 dB at frequencies in the range of 2000-2500 Hz for exposure times of anywhere from 2 to 5 seconds or longer. The objective of this research is to further develop the theory of acoustic agglomeration, particularly for conditions existing in the flue gas of coal-fired power plants (atmospheric pressures and temperatures up to 700°F). Another area of investigation deals with basic acoustic investigations, such as nonlinear acoustic studies with particular emphasis on acoustically generated turbulence and acoustic-absorption characteristics for products of combustion. The overall objective is to improve the capability of existing equipment (i.e., baghouses and ESP's) to capture the fine respirable particles (<2 microns).

Moving of test equipment into a new laboratory was just recently completed. As a result of extensive studies at the Pennsylvania State University, it was determined that siren-type sound sources offer the greatest promise of meeting the efficiency, reliability, and cost requirements for acoustic agglomerators. An extensive study was begun to develop the technology for the design of high efficiency sirens that will have the flexibility and control capability needed for acoustic agglomerators. An analytical model of the siren's acoustic energy generation processes was developed and is being tested against prior experience with existing sirens. A flexible siren test fixture was also designed with various ideas and prospects for the design of high efficiency sirens, utilizing both aerodynamic and acoustic phenomena to enhance the acoustic energy generation process. Tests will begin during mid-summer of 1984. (Pennsylvania State University)

Study of the E-Beam Precharging for Improved Capture of Fine Particles in an Electrostatic Precipitator

The objective of this research is to study the theory of improving the capture of fine respirable particles (<2 microns) by precharging the particles using an electron beam before they enter an electrostatic precipitator. A secondary objective is to study whether such a precharger is compatible with the existing E-Beam combined NO_x/SO_x processes.

The first particle-charging experiments with the new Mark I precharger in the Florida State University Electron Beam Precipitator Test System confirmed the abundant production of ion currents by electron beam ionization and clearly showed that the electron energy must be matched with the electrode geometry for effective particle charging.

A bench-scale precharger specifically designed to match the electron energy with the electrode geometry has been constructed, and effective particle charging has been demonstrated. In the bench system experiments with bi-electrode and tri-electrode geometries, the effects of electron beam energy, beam current, DC and pulsed electric field strength, current density, and exposure time on charging efficiency were investigated by measuring the charge acquired by both large conducting spheres and 1- to 3- μ m-diameter polystyrene latex aerosol particles. A 90-keV electron beam source was constructed for this purpose.

The next step in the assessment of electron beam prechargers in two-stage precipitator systems for the control of fly ash from coal combustion is the incorporation of an energy-geometry matched electron beam precharger in the Electron Beam Precipitator Test System. The 90-keV electron beam source will be used in Mark II precharger tests that are scheduled for the next quarter. Other interesting spin-off concepts, including one that suggests that a new and novel method for SO₂ control may have been discovered, will also be continued during the next quarter. (Florida State University)

Study of Integrated Environmental Control for Coal-Fired Power Plants

Recently, the concept of integrated environmental control has emerged in the electric power industry, based upon improved understanding of the couplings and interactions of power plant mass and energy flows, including environmental waste streams. Relative to the "piece-meal" approach to environmental controls that has characterized past developments, integrated environmental controls based on a total view of the power plant system offers the potential for improving plant performance, lowering costs, and reducing adverse "cross-media" environmental impacts that often occur when a problem is simply moved from one environmental medium to another (e.g., water and solid waste problems caused by an air pollution control system).

At the same time, new processes for the cleanup of emissions from coal-fired power plants have been under active development by the U.S. Department of Energy and others. These technologies encompass various means of pre-combustion, combustion, and postcombustion controls, including systems for the simultaneous removal of more than one pollutant. Many hold promise of reducing pollutant emissions more ef-

fectively and/or economically than with conventional technology. How advanced technologies might best be used or combined to optimize environmental control system design is the subject of the present research.

Research Objectives

The objective of this research is to develop a computerized modeling and assessment framework for integrated environmental control systems employing conventional or advanced technologies. The effort is divided into four principal tasks:

- Development of an integrated systems' model suitable for analyzing conventional and advanced technologies in a way that is systematic, comprehensive, and flexible
- Base-line studies of integrated environmental control system designs based on conventional technologies
- Development of preliminary technical and economic models of selected advanced processes currently under development
- Comparative assessments of integrated environmental control systems based on advanced process technologies

To date, a prototype model has been assembled of a coal-fired power plant that contains flexible modules for precombustion, combustion, and post-combustion environmental control systems components. Performance and cost models also have been developed and implemented for most of the conventional base-line components. These include models of physical coal-cleaning plants (for both sulfur and ash removal); combustion-based NO_x controls; electrostatic precipitator and fabric filter particulate collectors; wet limestone and dry lime (spray dryer) FGD systems; and untreated ponding of landfill solid-waste-disposal systems.

Preliminary testing of the integrated model has recently been started. The model has also been implemented in a newly developed software system, called DEMOS, which offers a powerful and sophisticated tool for analyzing the propagation and effects of uncertainty. This will be especially useful in later work involving advanced technologies, which, by their very nature, will tend to have large uncertainties in many technical, environmental, and economic parameters. The effect of key uncertainties in both conventional and advanced designs will be an important element of the integrated systems studies to be performed

as part of this research. Completion of the base-line models and studies is expected in September 1984. (Carnegie-Mellon University)

Simultaneous SO_x/NO_x Control for Low-Rank Coals

The overall project objective is to develop an economical process for simultaneous control of 90% of the SO_x/NO_x emissions derived from combustion of low-rank coals. The key to accomplishing this goal is the development of a dry process readily adaptable to retrofit situations and useful in areas of the West where water supplies are scarce. Present work involves the direct injection of a calcium-based sorbent material, with subsequent collection of flue gas particulate (including the calcium-based sorbent material) in a high temperature baghouse ($\sim 1000^\circ\text{F}$). Use of a catalytic or noncatalytic NO_x reduction step in conjunction with the high temperature baghouse provides for simultaneous control of SO_x/NO_x emissions.

Tests to date indicate that pressure-hydrated lime may overcome many of the problems encountered earlier using limestone for direct boiler injection for SO_2 control. A full-scale demonstration using pressure-hydrated lime is planned on the same boiler in which tests were made earlier using limestone injection. This should give a direct comparison of the two reactants under similar operating conditions. (University of North Dakota Energy Research Center with Grand Forks Project Office)

Thermodynamic Data for Combined NO_x/SO_x Removal Processes

The objective of this project is to provide reliable thermodynamic data on SO_x , NO_x , and SO_x/NO_x processes for use in the selection, design, and optimization of flue gas cleanup systems.

The approach adopted for this work is to compile and evaluate existing thermodynamic measurements and from there to develop recommended values for thermodynamic properties, values that reproduce well the best measurements. Maximum use is made of existing data and existing evaluations. Where necessary, estimates are made. If appropriate, suggestions are made for new measurements. (The present project does not have an experimental component.)

A good start has been made during the past year in developing and assembling the data base required to meet the project objective. The slow,

laborious task of gathering and assessing the required data will be continued during the next quarter. (National Bureau of Standards)

Additive Effects of Scrubber Chemistry

Wet flue gas simultaneous desulfurization and denitrification processes were developed by the Japanese in the 70's and have been shown to be very efficient in SO₂ and NO_x removal (more than 80% for both gases). However, these wet processes have not reached the commercial stage yet because they are uncompetitive economically. The most promising type of wet process developed so far is based on the addition of ferrous chelates in scrubbing liquor to enhance the absorption of NO by forming nitrosyl ferrous chelates in aqueous solutions. Nitrosyl ferrous chelate can then react with dissolved SO₂ to produce N₂, N₂O, dithioate, sulfate, and various N-S compounds, while some ferrous chelate is oxidized to ferric chelates, which are inactive. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N-S compounds from the solutions, and

reduction of ferric chelate back to ferrous chelates. The chemistry of this type of process is complicated and has not been investigated well.

The objective of this research project is to study the kinetics and mechanisms of important reactions involved in this type of process in order to determine an optimum process design and operating conditions, as well as to investigate the chemical reactivity of SO₂ and NO_x for the development of efficient catalysts and/or additives for use in flue gas scrubbers to control both SO₂ and NO_x efficiently and cost effectively.

Efforts to date have identified promising chelates with high activities and have eliminated some of the problems encountered earlier in Japan with these types of processes, including high catalyst losses and high water-evaporation losses. Substantial interest by vendors has been shown in these results, and pickup in this area can be expected to result in attempts to commercialize processes based on some version or adaptation of these types of wet processes that could become cost competitive with other options. (Lawrence Berkeley Laboratory)

COAL PREPARATION

R.E. Hucko, Cost Account Manager

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It is the objective of this activity to promote the widespread acceptance of coal preparation as a pretreatment step prior to coal utilization. The objective is being achieved through contract research in the subactivities of coal characterization, beneficiation (both chemical and physical), and ancillary operations.

Coal Characterization

The objectives of this task are to (1) determine the effects of stage crushing on the liberation of ash, pyritic sulfur, and other impurities on coals crushed down to 44 microns, (2) develop a coal-pyrite-size data bank and attempt to correlate pyrite size with sulfur reduction, (3) determine mineral particle quality, size distribution, and degree of association with coal macerals, (4) identify and evaluate the association of trace elements with specific mineral forms in the products from advanced coal-cleaning processes, and (5) determine the ashing properties of components of deep-cleaned coals in order to predict the synergetic effects of blending such coals.

Separation and Fluorescence Characterization of Coal Macerals

The objective of this project is to establish a laboratory to separate and characterize coal macerals. Approximately 95% of the equipment for the laboratory has been obtained and is functional.

As a result of the significant loss (approximately 92%) in coal material during the nitrogen mill grinding process, consideration has been given to the construction of a controlled-atmosphere grinding chamber with more standard equipment. In the interim, two coal samples from Southern Illinois University's (SIU) Coal Characterization Laboratory sample bank were ground at Argonne National Laboratories. The first sample is a paper coal from the Illinois Basin with about 7% cutinite, and the second sample is a commercial enrichment of resinite from the Hiawatha seam in Utah. Demineralization and solubilization processes have been carried out on these preground samples. In addition, three small-scale density

gradient runs have been performed successfully employing a swinging-bucket rotor (run time was 30 minutes at 10,000 rpm). Experimentation is underway using a method of forced pressure filtration through selective membranes in order to minimize the time that the coal samples are in contact with air. Preliminary results have shown this method far superior to more traditional gravity filtration procedures. Experimentation has also begun in preparing the samples for fluorescent microscopy using different films and methods. Presently, 0.1 mg of purified maceral sample is being suspended in 0.5 mL of a 0.5% polymer solution and dried down into a 1-cm-diameter circular spot on a rectangular cover slip. This allows for several sample areas to be prepared for fluorescent analysis. (Southern Illinois University)

Microchemistry of Illinois Coal: Impact for Sulfur Removal

The purpose of this research effort is to investigate the impact that the removal of sulfur has on the microchemistry of selected Illinois coals.

To this end, significant data have been collected via the electron microanalyzer and differential thermal analysis (DTA) of the GRI reference samples of Illinois No. 6 coal, as well as of selected samples of Illinois No. 5 coal. Sulfur content of the GRI sample coal has been determined to be about 1.2%, which is too low to provide good data on the distribution of sulfur among different macerals. Therefore, another sample of Illinois No. 6 coal with higher total sulfur will also be used for the complete schedule of characterization tests. The microprobe instrument is now providing reliable and reproducible data, as seen by statistical checks. Data on C, Ca, S, Fe, and Si have been collected for vitrinite in Herrin No. 6 coal. Data are also now available to characterize the GRI samples in bulk, and these data tend to confirm preliminary average results for microanalysis. (Southern Illinois University)

Fine Coal Gravimetric Evaluations of Alaskan Coals

Float-sink testing of fine coal has been evaluated and reported for seven Alaskan coal samples. However, the data show some anomalies in the yield-ash relationships for the float-1.30 specific gravity products of the samples crushed to 65-, 200-, and 325-mesh top sizes. For example, a test completed on a sample of Waterfall bed coal, using ZnCl as a separating medium, showed decreased weight recoveries and higher ash con-

tents when compared to similar tests using heavy organic liquids. Therefore, additional tests are being conducted using surfactants, reverse float-sink procedures, other heavy liquids, and drying techniques to resolve these anomalies. (University of Alaska)

Fine Coal Characterization Evaluations of Western Region Coals

Centrifugal float-sink testing is continuing on Western Region coal samples crushed to 5-mesh top size. Washability analyses will be reported as soon as chemical analyses are received and the data evaluated. Some float-sink testing is also being done on samples crushed to 200-mesh top size. Samples of the float-1.30 specific gravity products will be evaluated on a yield-ash basis to obtain preliminary trends in order to determine if the float-sink testing is progressing properly. Yield-ash relationships will be plotted to determine if there are any anomalies in the data. (University of North Dakota Energy Research Center)

Gravimetric Evaluations of Southern Appalachian Region Coals

Raw coal channel samples have been collected from the Pocohontas No. 6, Sewell, Beckley, and Fire Creek coal beds in southern West Virginia. Gravimetric evaluations have been completed on each sample crushed to 65-mesh top size. The Fire Creek coal bed sample, as shown in Table 6, was evaluated at 65-, 200-, and 325-mesh top sizes.

The data show a slight improvement in ash reduction when crushing to 200-mesh top size, but there is a considerable decrease in yield for the float-1.30 specific gravity product. When crushing to 325-mesh top size, the ash actually increases in the lighter specific gravity fractions. Tests are being conducted to try to determine the reason for these anomalies. (Commercial Testing and Engineering Company)

Identification and Evaluation of Mineral Forms in Washed Coals

Low-temperature ashing of the selected coal samples and fractions is continuing. Additional samples were ashed from the Kentucky No. 9 seam, which has a high carbon content.

During the quarter, operational problems were experienced with the Phillips X-ray Diffractometer. Premature failure of the X-ray source tube at 300 hours delayed the unit's use until the

Table 6.
Cumulative Data, Percent

	65 mesh x 0		200 mesh x 0		325 mesh x 0	
	Wt.	Ash	Wt.	Ash	Wt.	Ash
Float 1.30	32.3	1.1	6.2	1.9	4.3	1.1
1.30 x 1.40	80.2	1.8	72.9	1.6	79.6	2.0
1.40 x 1.60	89.6	2.9	89.6	2.8	90.3	2.9
Sink 1.60	100.0	9.6	100.0	9.5	100.0	9.0

manufacturer installed a new tube. In turn, the new tube necessitated redetermination of the X-ray patterns (diffractograms) for the standard mineral reference samples. The purpose of the rerun was to establish the base-line drift at the quarter angles of incidence.

An adaptation of the method of F.H. Chung is being developed for the quantitative evaluation of the LTA coal ashes being produced. This method uses calculated standard intensity (k) values that are dependent on (1) the instrument being used, (2) the crystalline nature of the component, and (3) the crystal plane selected. The matrix is not a dependent factor. (Bituminous Coal Research)

Microcharacterization of Mineral Matter Components in Coal

Work has proceeded on interfacing the upgraded Automated Image Analysis (AIA) system to the X-ray analyzers. A first version of the assembly language communication routines has been written and is undergoing testing and refinement. The interface should be finished and the upgrade completed with the next quarter.

A study was performed on the reproducibility of AIA results. Five pellets each of three coals were analyzed for approximately 1500 particles. The AIA estimates of the mineral matter fraction were found to have coefficients of variation (standard variation/mean) of less than 20% for minerals that made up more than 10% of the mineral matter. The coefficient of variation rose quickly for minerals making up less than 5% of the mineral matter.

Samples of Pittsburgh bed, 200 mesh x 0 raw coal, a 1.3 specific gravity float fraction, and an Illinois No. 6 bed, 60 mesh x 0 raw coal were subjected to hot and cold nitric acid leaches per ASTM specifications. Residues were then analyzed by AIA to determine the pyrite fraction of the

mineral matter. Preliminary results show the cold nitric acid leach to be much less effective in removing the pyrite. Pyrite fractions in the cold-leached samples ranged from 5% to 14% of the total mineral content.

Work in the next quarter will focus on finishing the AIA upgrade, beginning coal/mineral matter association studies, and wrapping up work on the nitric acid leaches. (Ames Laboratory, Iowa State University)

Ashing Properties of Deep-Cleaned Coals

Data that Ames has collected on low-temperature-ashing residues from coals suffer from lack of comparison of data collected from high-temperature-ashing experiments. Therefore, high-temperature ashes are now being obtained on the same coals that were previously used for low-temperature-ashing experiments. Two high-temperature furnaces have been set up, one for forming ash from coal directly at ASTM-specified conditions and another for heating low-temperature-ash concentrates to higher temperatures.

Studies continue on ashing coals and blends of coals at low-temperature conditions. Work concerning the improvement of low-temperature-asher design is continuing with excellent results. Qualitative low-temperature-ash concentrates are now prepared in less than 10% of the time formerly required for this procedure.

Standardless quantitative X-ray diffraction analysis experiments are continuing. A new attempt at reducing the error margin is in progress. It is the aim of this project to reduce the relative error from the present 5% down to 3%.

Experiments on high-sulfur coals burned in the presence of calcite indicate that finely ground calcite burned with the coal will capture approximately 50% of the sulfur in the ash as the infusi-

ble calcium sulfate anhydrite. It appears that this technique, perhaps combined with introduction of trona or nahcolite into the exhaust stream, may yield good results. (Ames Laboratory, Iowa State University)

Photoacoustic Spectroscopic Analysis of Fine Coal

Research has concentrated on testing the applicability of the Fourier Transform Infrared-Photoacoustic Spectroscopy (FTIR-PAS) method for analyzing the oxidation state and mineral character of coal during beneficiation. Additional work has been done in developing sampling methods needed for the above applications to work.

Two important results have been obtained that have potential applications in coal preparation:

- a. The FTIR-PAS method can produce data on a coal sample that correlate well with results from a number of standard characterization tests that require substantially more analysis time.
- b. The FTIR-PAS data provide simultaneous information on organic and mineral components of coal. In the case of the Gravimelt desulfurization and demineralization process, this should allow the monitoring of the trade-off between mineral removal and loss of heating value monitored on the same specimen by using the photoacoustic infrared absorption spectrum. (Ames Laboratory, Iowa State University)

Coal Beneficiation

The objective of this task is to develop and improve physical and chemical coal-cleaning processes to extract a maximum proportion of the ash and sulfur from U.S. coals.

Development of System Operating Parameters for Ash and Sulfur Reduction in Illinois Basin Coals by Froth Flotation

The objective of this project is to develop froth flotation system optimization parameters via bench-scale testing and to begin pilot-scale froth flotation tests. As scheduled this quarter, bench-scale testing using a 2000-gram Denver D. type froth flotation cell has continued in order to optimize reagent concentrations and cell-operating parameters. A series of 27 tests has been conducted on five of the six channel samples obtained from selected coal mines operating in south-

ern Illinois. Three series of data pertaining to three different mines have been optimized using a nonlinear statistical computer model. The results of a series of tests conducted on a coal sample obtained from a mine operating in the Illinois No. 6 seam indicate that it is possible to reduce the total sulfur in the sample from 4.48 to 1.51 with a coal recovery of over 70% in a single-stage flotation. A similar series of tests performed on another southern Illinois coal resulted in a total sulfur decrease from 3.56% to 1.61%, with a coal recovery of 71%. Similar results of total sulfur reductions and coal recoveries have been obtained with the other samples tested.

A Denver, 8-cell, No. 8 Sub-Aeration, cell-to-cell, pilot-plant froth flotation machine has been installed in the ground control building of the Coal Technology Laboratory in Cartersville. The unit has a continuous capacity of 500 lb per hour and pulp volumes of 2.75 cu ft per cell. Initial tests on the flotation machine have already begun. Batch-type tests are being conducted initially with the optimized values of the reagent concentrations as determined from the bench-scale tests. (Southern Illinois University)

Electrochemical Desulfurization of Coal Slurries

The objectives of this investigation are to (1) electrochemically desulfurize the coal slurries and (2) simultaneously produce valuable hydrogen gas at electrode potentials lower than the potential required for ordinary water electrolysis.

During this quarter, coal slurries were electrolyzed under potentiostatic conditions at electrode potentials ranging from 1.2 to 1.3V, SCE. Multivalent cations of Ce (IV) and Fe (III) were added to Colchester No. 2 coal slurries electrolyzed on a Pt electrode at 65°C. Depending upon the reaction conditions employed, sulfur removals were as high as 53%, while a decrease of about 50% in ash content was observed. It is interesting to note that the addition of Ce (IV) and Fe (III) to the coal slurry accomplishes greater sulfur removals than the sulfur removal obtained by the addition of Ce (IV) only. Further, it is shown that at low concentrations of Ce (IV) (low-oxidizing conditions), smaller coal particles resulted in higher sulfur removals and current densities; however, at higher Ce (IV) concentrations (high-oxidizing conditions), greater sulfur removal and currents were observed for larger coal particles.

In addition to sulfur, significant ash removals (18% to 50%) via electrolysis were also obtained. (Southern Illinois University)

Characteristics of a Hydrocyclone with Raw Material Input Along the Central Axis

The objective of this project is to determine if a hydrocyclone with the raw solid material input along the central axis performs better than a conventional hydrocyclone. A major accomplishment this quarter was the acquisition of sufficient data using the mechanical-auger-type central-feeding device to make a determination that this is not a feasible means of inputting the raw material along the central axis. Conclusions from examining all the data are as follows:

- a. As the distance between the top of the auger and bottom of the vortex finder decreases, more solids report to the overflow.
- b. At a given setting of the auger feeder, the amount of solids to the overflow increased with increasing sphere size. This is generally true with tangential input of spheres as well.
- c. The auger speed has a definite influence on the percent of solids reporting to the overflow. At faster auger speeds, a larger number of spheres reported to the overflow. In general, changing the speed of the auger has a major effect on the separation of the spheres.
- d. Tangential feed experiments were carried out both with the auger running and with it turned off. In general, fewer spheres reported to the overflow when the auger was turned off, but there was not a significant change noted in the results.
- e. A comparison of the tangentially fed spheres to the centrally auger-fed spheres for a given specific gravity shows large amounts of spheres reporting to the overflow for the tangential feed.
- f. The tangentially fed sphere data show much better (sharper) splits than when the spheres are auger-fed along the central axis. Also, the tangentially fed sphere data are significantly more consistent. (Southern Illinois University)

True-Heavy-Liquid Beneficiation

The objective of this project is to develop an efficient process for cleaning 28 mesh by 0 coal utilizing a true-heavy-liquid as a separating medium in a cyclone.

The testing this quarter consisted of four more heavy-liquid cyclone runs (Nos. 5, 6, 7, 8), a series of centrifugal float-sink tests, and two series of froth flotation tests done at PETC. The data in Table 7 have been updated since the last quarter.

The remainder of the data will appear in the final report. The main variables examined in the last four tests were (1) surfactant loading, (2) low heavy liquid specific gravity, and (3) ultrafine feed size, as Table 7 shows.

A series of centrifugal float-sink tests at various moisture contents were run because of the anomaly between tests 1 and 2. Although their operating conditions differed by only 0.3% moisture, the performance results for test 2 were significantly worse. Preliminary centrifuge tests showed that separation performance may be sensitive to small changes (on the order of 1%) in moisture content.

Finally, two series of froth flotation tests were run at PETC on 28 mesh by 0 and 220 mesh by 0 samples for a direct comparison with the heavy-liquid cyclone. It appears that the heavy-liquid cyclone can produce an improved grade/recovery relationship over froth flotation, with the attendant advantage of almost two orders of magnitude greater throughput capacity per unit of volume.

All of the test work and analyses for this contract were completed this quarter, and a draft final report was recently received. It will be reviewed by DOE, revised by Otisca, and then published by TIC. (Otisca Industries, Ltd.)

Liquid CO₂ Coalescence (LICADO Process)

The overall objective of this project is to develop a novel coal-cleaning process that will produce superclean coal containing less than 1% ash by selectively coalescing ultrafine coal with liquid carbon dioxide.

During this quarter, additional test runs were conducted using the 1-inch test pressure cell with an improved sampling system. Three different size fractions, minus 200, minus 35 mesh, and 100 by 200 mesh, of Upper Freeport bed coal with an initial ash content of 27% to 34% were used for the experiments. All runs were carried out at room temperature and at a pressure of 850 ± 50 psig. Two different slurry concentrations, 13% and 24%, were tested. The results are summarized in Table 8.

For the minus 35 mesh coal, the experimental values of clean coal and refuse ash content, as well as the product yield, are in general agreement with results reported in the last quarterly. On the other hand, the data showed that the 100-by 200-mesh coal yielded a much better separation (separation index > 2.0), while the minus 200-mesh coal gave a significantly worse

Table 7.
Preliminary Results of Heavy-Liquid Cyclone Tests

	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>	<u>Test 4</u>	<u>Test 5</u>	<u>Test 6</u>	<u>Test 7</u>	<u>Test 8</u>
Coal Size, mesh	28 x 0	28 x 0	28 x 0	28 x 0	28 x 0	28 x 0	400 x 0	28 x 0
Surface Moisture, %	1.8	1.5	10.0	10.0	17.2	10.5	6.0	15.0
Solids Concentration, %	20	10	10	10	10	10	20	10
Inlet Pressure, psi	85	85	85	85	85	85	85	85
Coal Feed Rate, tph	3.5	1.75	1.75	1.75	1.75	1.75	3.5	1.75
Additive Concentration, lb/ton	0	0	0	10	20	10	10	20
Clean Coal Ash, %	7.2	13.0	18.2	7.2	21.5	3.2	24.2	
Refuse Ash, %	78.7	82.3	66.7	83.7	79.5	53.8	72.4	
Clean Coal Yield, %	68.1	75.3	78.9	70.1	83.5	48.8	83.4	
Efficiency Index	744	478	289	814	308	820	250	
S.G. of Separation	1.62	1.74	1.84	1.68				
Probable Error (Ep)	0.045	0.139	0.204	0.065				

*Test run with 1.30 specific gravity liquid.

Table 8.
Test Results for LICADO Process (Upper Freeport Bed Coal)

Size, Mesh	Feed Ash %	Solid Conc. of Feed Slurry, %	Clean Coal Ash %	Refuse Ash %	Yield %	Separation Index
Minus 200	29	13	22.6	39.3	70	0.67
	29	24	22.1	41.3	73	0.68
100 by 200	27	13	9.3	43.8	62	2.9
	27	24	11.6	53.1	77	2.0
Minus 35	34	13	18.0	69.9	86	1.5
	34	24	16.0*	77.6*	90*	1.8

*Comparable values reported in last quarterly are 14.0, 80.5 and 91, respectively.

separation (separation index < 0.7) than the minus 35-mesh coal (separation index ranging from 1.5 to 1.8).

The relative abundance of ultrafine ash particles and their entrapment in the clean coal product are believed to be the most probable causes for observed variations in separation efficiency for the three different size fractions. Further confirmation of these findings will be sought by using a micrographic technique coupled with low-temperature ashing to determine the size distribution of ash particles in the clean coal and refuse samples.

The design of the larger, second-generation, 3-inch-i.d. test cell with mechanical agitation was completed. Procurement of parts, and fabrication have begun. The unit is expected to be ready for testing early next quarter. (University of Pittsburgh)

Mechanisms for Selective Coalescence

Several carbonaceous materials that may serve as useful models for coal were characterized by various techniques. These materials included Ceylon graphite and two types of carbon black. The graphite was highly crystalline and had an ash content of only 0.393%. The equilibrium contact angle for the graphite was $60 \pm 3^\circ$ at the air/water/solid interface at room temperature, regardless of crystal orientation. The graphite was readily wetted by heptane. The carbon blacks were very pure, noncrystalline, submicron-size powders. The zeta potential of fine particles of the carbonaceous materials suspended in water was measured at various pH levels. Over much of the pH range, one form of carbon black had a high positive surface charge, another form had almost no charge, and the graphite had a large negative charge. The pH corresponding to the isoelectric point was 9.5 for the first carbon black, 7 for the second carbon black, and 3 for the graphite.

A number of coalescence experiments were conducted in which carbon black or powdered graphite was suspended in water and then agglomerated with a liquid hydrocarbon at room temperature. In some experiments, powdered kaolin was mixed with the carbonaceous material beforehand. The hydrocarbon liquids included heptane, toluene, mixed xylenes, cyclohexane, and No. 2 fuel oil. The carbonaceous particles were readily agglomerated by either heptane or No. 2 fuel oil and subsequently recovered at high yield by screening the suspension. Somewhat lower recoveries were obtained when kaolin was mixed with the carbonaceous material and/or

other hydrocarbon liquids were employed. When powdered graphite was agglomerated with heptane in suspensions adjusted to various pH levels, the maximum recovery of agglomerated material was achieved when the suspension was at or near the isoelectric point. (Ames Laboratory, Iowa State University)

Fused-Salt Process Development

During this quarter, the Gravimelt process emphasis has centered on the design, fabrication, and installation of the new countercurrent flow reactor system. The system consists of four coal-caustic leachers and a caustic melt tank, all of which are fabricated of nickel. It is capable of processing 20 pounds of coal per hour. The reactor system was fully installed and checked out with shakedown tests for each of the repository coals. The shakedown operation gave information on (1) time required for the coal to separate from the caustic upon the interception of stirring, (2) operational sequencing for the movement of coal from reactor 1 through reactors 2, 3, and 4, and out of the reactor, (3) movement of caustic from the melt pot through reactors 4, 3, 2, 1, and then to the spent caustic receiver, and (4) deforming requirements. TRW has begun negotiations with three major aluminum companies, namely, Kaiser Aluminum and Chemicals, Martin Marietta Corp., and Reynolds Aluminum, regarding applications, by these major aluminum producers, of Bayer alumina chemistry to the regeneration of spent caustic from the Gravimelt leacher. One-pound samples of spent caustic from the countercurrent leacher equipment have been distributed to each aluminum company for their initial evaluation. TRW hopes to select one of the companies and award a subcontract for the development of a caustic regeneration scheme.

In addition, the attempts to regenerate spent caustic using a nonaqueous and non-Bayer chemistry have shown promising early results. This work currently is being conducted under company funds but will be incorporated into the program if it offers advantages over the aqueous approach based on the aluminum industry technology.

The recovery of alkali ions and acid from the cleaned-coal wash stream using electrolysis, ion-exchange resins, and calcium formate precipitation have been investigated.

Tests of the newly installed basket filter showed that the dirty caustic cannot readily be separated from the coal by filtration. This verifies the earlier results that showed that either pressure-

filtering or centrifuging the slurry was necessary. Studies on the separation of cleaned coals from various process streams will be done using coal from the countercurrent reactor. (TRW)

Regeneration of Alkali in Caustic Desulfurization Systems

Phase diagram studies on the Na_2S - NaOH and the Na_2CO_3 - NaOH binary systems have been completed, and papers describing the results have been submitted for publication. The data are being used in evaluating the spent molten caustic system used in the desulfurization of coal.

The study of the reaction of molten NaOH with pyrite (FeS_2) at 350°C has also been completed. Using X-ray diffraction data, the principal products have been identified as Na_2S and NaFeO_2 , with small amounts of Na_2S_2 also detected. In the presence of hydrogen or a reducing atmosphere, such as found during the treatment of coal, the overall reaction is postulated as follows:

with Gibbs free energy change of -100.8 kJ at 600K . In the absence of hydrogen or a reducing atmosphere, the overall reaction is postulated as follows:

with Gibbs free energy change of -90.8 kJ at 600K .

Additional experiments were performed to improve the sulfur balance during the treatment of coal with molten caustic and the subsequent work-up of the caustic solutions. Generally, only 70% of the sulfur can be accounted for in the solids and solutions produced. However, preliminary experiments using a sulfur scavenger to precipitate additional sulfur improved the sulfur balance to $\sim 99\%$. Further tests are being planned to confirm and explain these results.

The use of aqueous NaOH of various specific gravities as heavy media in float-sink precleaning of coal is also in progress. The float fractions have been analyzed for moisture, ash, and total sulfur. Cold- and hot-water washing and acid washing of the recovered coal were used to check for sodium incorporated in the coal.

As another regeneration scheme, the reaction of solid Na_2S with CaCO_3 at high temperatures was studied. At 650°C , only a small amount of CaS was produced; but at 800°C , CaS was the predomi-

nant product. (Ames Laboratory, Iowa State University)

Trace Element Removal

Two coals, one from Illinois and one from Pennsylvania, high in ash contents, were used for the main study of this work. Each coal sample underwent acid treatment, but only the Illinois coal was used in the dimethylsulfoxide (DMSO) treatment. Except for DMSO treatments, it was assumed that the coal organic material is not altered by this process, although it is known that HNO_3 oxidizes organic materials and nitrates coal specifically. The raw and leached coals were analyzed for numerous trace elements using X-ray fluorescence, inductively coupled plasma, atomic absorption, and ion-selective electrodes.

The analyses on the Illinois No. 6 coals treated with HNO_3 or distilled water have been completed. Due to uncertainties in the analytical data, no definitive conclusions could be drawn about the removal efficiencies for many of the elements. However, it is evident that levels of Fe, Mn, Pb, and Zn were reduced by 75% or more as a result of hot HNO_3 leaching, while levels of Be, Co, Ni, Se, and V appeared to decrease by lesser amounts. Although the hot HNO_3 usually had a somewhat higher extraction efficiency than the cold HNO_3 , the differences generally observed were not major. No significant reductions in trace element levels were observed for the coal leached with distilled water.

The HNO_3 , water, and HCl/HNO_3 extractions on the Lower Kittanning coal have also been completed. As with the Illinois No. 6 coal, water did not substantially reduce trace element levels. The most prominent reduction in trace element content resulting from the HNO_3 extractions was for As. Both the hot and cold treatments reduced As levels by about 90%, which correlated well with the 90% reduction in iron levels that was observed. Arsenic is commonly in solid solution with pyrite, the predominant iron-bearing mineral in coal; and major reductions in As levels are not surprising when the majority of the pyrite is removed. Small amounts of Ba, Be, Cd, Co, and Pb were also apparently removed. Extraction efficiencies of trace elements by the hot and cold HNO_3 treatments were generally comparable.

Unlike the HNO_3 -only extractions, the HCl extractions followed by HNO_3 extractions resulted in significant improvements in reductions of some trace element levels. Reductions of other trace elements were less pronounced.

For the coal leached with DMSO, no definitive conclusions could be drawn in regard to trace element removal. Although some concentration reductions were observed, a total sulfur analysis of one of the treated coals (after heating to remove H₂O and DMSO) suggested that DMSO was still incorporated in the coal. Thus, quantitative evaluation is as yet impossible. (Ames Laboratory, Iowa State University)

Microwave Interaction with Coal

Progress has been achieved in all four major areas of this study.

A. Experimental Microwave Applicator System

Materials have been purchased and construction of the Ames Laboratory Experimental Microwave Applicator System (EMAS) has begun. The EMAS includes the applicator resonant cavity, the choke assembly sections at both ends of the resonant cavity, the fused quartz applicator tube assembly for inert gas supply and discharge during irradiation, the coal treatment boats, and the apparatus support frame assembly.

B. Microwave System

The applicator is patterned after that described by Zavitsanos et al. It is a cylindrical tube operating in the TM₀₁ mode. Microwave energy is fed into the applicator through an iris in the wall of the tube. The ends of the tubes are equipped with "traps" so all the microwave energy will be contained within the applicator, and no radiation will escape from these openings. To provide the most favorable conditions for heating, the source (microwave generator and associated waveguides required) must be "matched" to the load (the cylindrical tube containing the coal).

C. Literature Survey of the Mineralogy Interactions

Using literature data, the mineralogical changes that could possibly occur during the treatment of coal with microwaves and aqueous caustic were evaluated. The major coal-related minerals that have been included in this study were clays (mainly kaolinite, illite, and montmorillonite), pyrite, quartz, and carbonates. In order to evaluate the effectiveness of each stage of the microwave desulfurization process, the solubility and dissolution kinetics of each of the major minerals in concentrated-alkaline and dilute-acid solutions were considered. The preliminary assessment was used to analyze the results obtained by the G.E. research group and to propose future experiments at Ames Laboratory.

D. Experimental Procedures

The Senior Research Technician has continued to provide initial coal samples and coal-derived mineral samples in a prepared state for ultimate microwave treatment. The identification of process parameters has been completed. Parameters included for microwave treatment were power level, temperature, time, and field strength. Other parameters for the caustic treatment were sodium hydroxide concentration, temperature, and time. The identification of process parameters was enhanced by the development of the draft report entitled "Abbreviated Summary of the GE Microwave Coal Desulfurization Work." This summary focused on the experimental techniques employed in this process. (Ames Laboratory, Iowa State University)

Correlation of Beneficiation with Fine-Coal Properties

The crushing, sampling, and cleaning of the Illinois No. 6 bed coal were completed. The magnetite medium for the dense-medium cyclone was adjusted to 1.60 specific gravity while the Deister table was adjusted visually. Sixty percent of the feed was recovered as clean-coal product. Analyses of this material showed 6.7% ash and 0.71% pyritic sulfur, representing reductions of 66% and 69%, respectively. Composition and fusion temperatures were also determined for ash on the raw and cleaned coal samples.

Washability tests were completed for the Illinois No. 6 bed coal crushed to 3/8-inch and 14-mesh top sizes. The 100-mesh x 0 material was removed and float-sink tested using a centrifuge. The analytical data indicate that the liberation of mineral matter may not be complete. These data will provide a base for evaluating improved liberation and removal of mineral matter for the sample to be crushed to 325-mesh top size and finer.

Carbonate and hydroxyl content, and low-temperature-ash determinations are in progress. Specific surface and porosity measurements have begun on the clean-coal sample. A Quantasorb apparatus is being used for the surface area determinations and will also be used for density measurements. With this system, the amount of nitrogen carried in a stream of helium that is absorbed or desorbed from the sample is measured and used to calculate the surface area. The instrument can also be used to measure particle densities by measuring the volume of helium displaced by a coal sample placed in a calibrated cell. (Amax Extractive R&D)

Microbial Desulfurization

In order to demonstrate the ability of the acidophilic and thermophilic bacterium Sulfolobus acidocaldarius to desulfurize coal, it has been necessary to purify the cultures, develop methods for short-term maintenance, optimize growth in liquid cultures, and develop a solvent to deliver dibenzothiophene to the organism. A number of strains of Sulfolobus have been received and three active strains will be further studied in terms of growth under various temperature and pH conditions.

A comprehensive dilution-to-extinction experiment is being used for purification. The metabolic potential of this pure culture will be compared with that of the consortium from which it was purified. This procedure is useful when the organism cannot grow on a solid medium.

Cultivation of Sulfolobus on solid agar media has been difficult because the agar dries rapidly at the high temperature (70°C) required. Experiments with silica, partially hydrolyzed starch, Gelrite, and TIC-colloid No. 600 are underway. Desiccation has been reduced by incubating the plates in polycarbonate jars. Trypan blue has been added to achieve contrast.

Sulfolobus acidocaldarius can grow either heterotrophically or autotrophically. A stated goal of the project is to determine the optimal pH and temperature for both modes of growth. The rate of heterotrophic growth can be monitored turbidimetrically, since only the increasing numbers of bacteria contribute to increase the turbidity. Because the volume of culture needed for the measurements is only 10 mL and because numerous tubes accommodating this volume can fit into a single waterbath, the growth rates at several pH's and one temperature can be determined simultaneously. The limit on the technique is the number of tubes that can be handled practically. It is anticipated that the rates and extents of growth of four strains can be measured at six pH's and two temperatures in a two-day period.

Autotrophic growth cannot be measured turbidimetrically because the sulfur particles contribute to turbidity in an irregular manner. Growth is not readily measured by the oxidation of S to SO₄, since several components of the medium, including carbonate, phosphate, and calcium, interfere with the assay. Presently, biomass is measured by increase in protein. Two standard techniques are being used — the Lowry technique and the Coomassie blue technique. Pristane has been selected as a solvent to deliver diben-

zothiophene to Sulfolobus acidocaldarius. Cultures with and without pristane have been inoculated to determine if there are any adverse effects from the solvent. (Lehigh University)

Extraction and Desulfurization of Chemically Degraded Coal with Supercritical Fluids

The objectives are to (1) determine the effect of process variables on selectivity of desulfurization of coal with different solvents, (2) evaluate the fate of sulfur in product streams, (3) determine the effect of KOH treatment of coal on supercritical desulfurization, and (4) set up the continuous reactor system for kinetic study.

The data obtained this quarter was from 300-cc, batch-reactor, stirred autoclaves. The coal, previously dried and ground to the desired particle size, is charged to the reactor, and alcohol is added. Heating the stirred mixture to above the critical temperature of the alcohol results in a pressure in excess of the critical pressure of the alcohol. After reaction for a designated period (generally 1 hour), the reactor is cooled, and liquid and gaseous products are collected through a condenser system.

A complete set of experiments of supercritical desulfurization with methanol at different temperatures has been accomplished on three standard coals provided by the Illinois State Geological Survey. The rate of desulfurization with methanol is greater than that with ethanol at lower operating temperature and for higher organic sulfur content in coal. The effect is reversed at a temperature of 400°C or above. It is concluded that the temperature and the ratio of organic sulfur to pyritic sulfur in coal affect supercritical desulfurization with ethanol more than with methanol.

A desulfurization study of a coal with high organic sulfur was carried out at 350°C with various alcohols under supercritical conditions. Ethanol and tertiary butanol demonstrate better selectivities for desulfurization. One of the batch experiments was conducted to follow the course of sulfur removal during supercritical extraction. Both gaseous and liquid samples were withdrawn periodically during the process. Only trace amounts of sulfur compounds were found in the gas samples. All the sulfur materials either are in liquid phase or are precipitated out from supercritical ethanol as a solid. Gas chromatograph analyses also indicate that no detectable concentrations of sulfur compounds were in the liquid before and just after the ethanol reached supercritical state, even though many organic materials

(HPLC data) were in the extracts. The rate of sulfur removal increased significantly and then leveled off toward the end of the reaction.

Table 9 shows the data from a set of experiments to desulfurize coal with different types of alcohols under supercritical conditions. In the experiments, 40 grams of a coal with high organic sulfur (73% organic sulfur, 27% pyritic and sulfate sulfur) were mixed with 40 grams of alcohol, and the mixture reacted at 350°C for one hour under supercritical pressures.

The KOH treatment study has been continued this quarter. It was found that KOH contributes to desulfurization more at lower temperature (275°C) than at higher temperature (400°C). For an oxidized coal, KOH actually inhibits the supercritical desulfurization if ethanol is the solvent. The oxidation state of coal has little effect for supercritical desulfurization by methanol.

After initial pressure testing, the continuous reactor system has been moved to the Coal Technology Laboratory. The major system components include a coal/solvent slurry preparation tank with recycle pump; a variable-flow high-pressure pump; a two-liter, stirred tank reactor, and a product collection system. To avoid the high cost and operational problems inherent to small-scale pressure letdown devices, dual product collection chambers are being used that will operate at system pressure. (Southern Illinois University)

Ancillary Unit Operations

The objective is to develop new, improved ancillary unit operations for coal preparation plants to achieve the goal of supplying the optimum yield of deep-cleaned coal product of consistent quality.

Fundamental Study for Improvement of Dewatering of Fine Coal/Refuse

During this quarter, major efforts were devoted to the following three areas:

- A report on the effect of entrapped air bubbles on fine coal vacuum filtration was prepared and submitted for technical review. Quantitative correlations for the rate of filtration/dewatering and for the moisture content of dewatered filter cakes, in terms of air bubbles' size and volume percent of air bubbles, are given in the report.
- Further modification of the three-dimensional network model was accomplished by introducing "channels" in the network (i.e., correlation of pore/bond sizes in the direction of flow). The modified version of the model has been shown to provide a much improved prediction of the desaturation curves and to yield values of the final moisture content that are in excellent agreement with experimental data. Furthermore, this modification can be incorporated easily into the dynamic module to be used for calculating the filter cake permeability or the rate of filtration and dewatering.
- Extensive experimental tests were conducted to study the effect of multiple surface-active agents on the dewatering and washing characteristics of fine coal filter cakes. Particularly noteworthy are the results obtained in surfactant-washing experiments. For example, the moisture content of a minus 32-mesh Pittsburgh bed coal filter cake formed in the presence of MIBC (a nonionic frother reagent) was reduced from about 20% to as low as 6% when washed with the anionic surfactant Aerosol-OT.

Table 9.

Run No.	Solvent Used	% Sulfur Removed	% Coal Extracted	Selectivity
R-141	Methanol	34.4	19.0	1.80
N0032	Ethanol	35.4	13.2	2.68
N0051	Tertiary Butanol	32.8	7.5	4.37
N0056	Isobutanol	31.6	19.5	1.62
N0058	Secondary Butanol	29.5	18.7	1.57
N0069	n-Butanol	30.8	11.7	2.63

During the next quarter, a chemically pure surface-active agent, dodecyl-amine hydrochloride, will be used to study the effect of surfactants on coal surface properties in an effort to get a better understanding of the surfactant-assisted dewatering process. (University of Pittsburgh)

Ultrafine Grinding of Coal in an Attrition-Chemical Reactor

Two coals with different grindabilities, and clean fractions separated from these two coals at 1.80 specific gravity are being used for comminution studies in a Union-Process Model 1-ST attrition mill. The coals are (1) Illinois No. 6 coal, River King Mine No. 1 (Peabody Coal Company), St. Clair Co., Freeburg, Ill.; and (2) Upper Freeport coal, Alpine Mine (Island Creek Coal Company), Grant County, Bayard, W.Va. The Hardgrove grindability indexes of the coals and the float fractions are shown in Table 10.

While the size reduction of the float fraction of the Illinois No. 6 coal proceeded more slowly than the size reduction of raw coal, as would be expected by the lower Hardgrove grindability index, the float fraction of the Upper Freeport coal also proceeded more slowly than the raw coal in contradiction of the Hardgrove grindability index.

A computer program was written to calculate and plot the relationship between particle size (mean volume) and specific energy (kW-hr/ton) to give an indication of the energy and time required to attain a given size.

Higher coal-media ratios decreased the energy required to attain a given particle size but with a slight increase in the time. Slower rotational speed also decreased the energy required to attain a given particle size but with a significant increase in time. The ultimate size reduction attainable was also directly related to speed. (Ames Laboratory, Iowa State University)

Dewatering of Coal by Pressurized Electroosmosis

The Komline-Sanderson Model ZR-125 zeta potential determining apparatus arrived early this quarter. The instrument was installed and tested, and is now being used. The operating instructions were condensed for quick referencing while operating the instrument. A demonstration of the instrument for training purposes was conducted for potential users at Ames Laboratory.

A permeameter has been designed, and construction is well under way. The permeameter will be used to study the hydraulic conductivity or permeability of the ultrafine coal matrix with various degrees of consolidation and particle size distributions. These data will be used in optimizing and correlating the ultrafine coal suspension characteristics of the pressurized electroosmosis process and to develop empirical, and perhaps theoretical, equations for the pressurized electroosmosis process.

The design and debugging of the integrated circuit board for interfacing the research instruments and the computer have been completed. The computer programming for data acquisition is also underway.

A presentation was made for the Fossil Energy Program review on April 24, 1984. Also, a paper entitled "PED: Pressurized Electroosmotic Dewatering" was presented at the 96th Session of the Iowa Academy of Science on April 28, 1984

A manuscript entitled "Coal Sludge and Fine-Coal Suspension Dewatering by Pressurized Electroosmosis" was submitted for presentation at the 15th Annual Meeting of the Fine Particle Society and for publication in the International Journal of Particulate Science and Technology. (Ames Laboratory, Iowa State University)

Table 10.

Sample	Hardgrove Grindability Index	Moisture, %
Illinois No. 6 - Raw	62	9.1
1.80 Float Fraction	56	7.4
Upper Freeport - Raw	81	1.2
1.80 Float Fraction	93	1.1

Development of an On-Line Pyrite-Monitoring Instrument

Ames has completed a test on the effect of particle size on the analytical results obtained from the pyrite monitor. As was seen in the laboratory, there is an apparent reduction in pyrite content when particles larger than 40 mesh are in coal stream. Ames has concluded that they can operate with minus-48-mesh coal, but they can get more consistent results with coal ground to minus-60 mesh.

An effort is being made to make the pyrite monitor as user-friendly as possible. Ames has gone to the "menu-driven" format of operation, with only one letter responses needed to invoke any of the several options presented to the operator. Several methods are being tried to make the initialization of the instrument as automatic as possible. (Ames Laboratory, Iowa State University)

On-Line Alkali Monitor

The purpose of this project is to investigate the adaptability and applicability of the alkali monitor and analysis techniques, developed earlier for analysis of gaseous sample streams, to the problem of continuous on-line determination of sodium and potassium in process and product streams from chemical and other advanced coal beneficiation plants.

Alkali determinations were completed, using conventional analytical techniques, for samples of Pittsburgh No. 8 coal from the Grafton Coal Company, Churchville Pit, Lewis County, W. Va.

Numerous experiments were conducted with respect to identification of the procedures and experimental conditions most suitable for the introduction of dry, powdered coal to the alkali monitor. So far, the stability of the signals observed with introduction of dry coal has not been adequate for quantitative determination of the alkali elements.

The custom-made circular-slot burner previously employed by the alkali monitor was replaced with a commercially available machine cutting torch. Although a complete study of the analytical performance of the cutting torch was not conducted, it was used extensively during this quarter and performed as expected. It is far less expensive than the circular-slot burner, required far less operator attention, and does not require water cooling. (Ames Laboratory, Iowa State University)

Ultrasonic Comminution

Energy Minerals and Research Company has shown previously that ultrasonic coal grinding has a definite potential for reduced energy consumption when compared with conventional grinding techniques. The goal of this project is to ascertain whether this advantage can be translated from the laboratory to industrial application. In previous laboratory-scale work, a 5 1/4-inch resonant tube was employed for comminution tests with the auger array. A throughput of 7.5 lb/hr for grinding 80% minus 200-mesh coal down to a size consist of 80% minus 20 microns was obtained. Larger cylinders (9 inches and 20 inches) have now been vibrated successfully with ultrasonic input power, employing two different methods of force driving the resonant tube. Phase II of this contract will attempt to establish the scale-up criteria for grinder throughput as a function of resonant-tube diameter. Hypothetically, a lower scale-up exponent (1-2) would be anticipated for the ultrasonic auger array than for a conventional piece of grinding equipment such as a ball mill, since the particle breakage is occurring at the periphery of the resonant tube and not in the interior of the device.

It has also been proven that it is possible to activate tubes of a wide range of different diameters and lengths by using either of two methods. The first method is to slot the tube into equal sections such that the mass of the slotted section and the coupler between the transducer and the tube can be force driven at any desired frequency. In the case of larger diameter tubes, with low natural resonant frequencies, it is possible to force drive these tubes at a desired frequency provided that the frequency is a harmonic of the natural resonant frequency. Both methods will be investigated as potential design options for pilot-plant application.

The newly constructed laboratory-scale grinder has been set up and is now operational. Preliminary shakedown tests are now in progress. An experimental test matrix, developed with the assistance of Dr. Peter Luckie, of Pennsylvania State University, will be applied. The Bond work index will be evaluated as a function of array gap size, speed of rotation of the ultrasonic auger, ultrasonic power input, coal hardness, and wet vs. dry comminution of the feed. The tests will be performed on a relatively soft Upper Freeport seam coal and a relatively hard Illinois No. 6 coal. (Energy and Minerals Research Company)

*Ultrasonic Versus Mechanical Comminution
of Coal: Size, Shape, and Fracture
Characteristics of Resultant Particulates*

The major objectives of this study are to investigate the size, shape, and fracturing characteristics of ultrasonically comminuted coal and to compare and contrast the results with measurements and observations taken from mechanically ground coal from the same feedstock. Analysis techniques used included scanning electron microscope based automated-image analysis (SEM/AIA) and high resolution scanning electron microscopy.

Four samples of ultrasonically and mechanically comminuted coals have been provided by the Energy and Minerals Research Company, in addition to the Upper Freeport (ball mill and ultrasonic grinds) and the Illinois No. 6 (ball mill, hammer-mill, and ultrasonic grinds) samples presently in hand. The coals supplied by the Energy and Minerals Research Company (Upper Freeport and Illinois No. 6) will be ground by ball mill, hammer-mill, and ultrasonic methods, and will be submitted in graduated steps of reduction, the maximum size being 100% passing through 80-mesh screen. This will allow for the determination of the following: (1) Is there any appreciable change in size distribution as the size of the coal is reduced? (2) Is there any physical size or shape change caused by reducing the product size? (3) What are the physical and/or chemical differences between ultrasonically ground coal and coal ground by current state-of-the-art methods? In addition, the Energy and Minerals Research Company has constructed two ultrasonic grinders of different mechanical construction, and an attempt will be made to determine if there is any difference in the products from the two processes.

During this quarter, four coal samples were analyzed by SEM/AIA, including Upper Freeport (<80 mesh, ultrasonic roller/coupler), Upper Freeport (<80 mesh, ball mill), Illinois No. 6 (<200 mesh, ball mill), and Illinois No. 6 (<200 mesh, hammermill). An additional sample (Illinois No. 6, 30-micron gap, ultrasonic roller/coupler) was analyzed last quarter. Approximately 2,500 particles were measured from each sample. Data collection time is approximately 1.5 weeks per sample. The particle size and shape data were analyzed by the SEM/AIA system's on-board computer and were also transferred to SIU's IBM 370/158 mainframe for additional processing. Five computer programs were written to produce the histograms and some of the statistical data.

Size distributions obtained for the Upper Freeport (ball mill) and the Upper Freeport (ultrasonic) samples are very similar to distributions for the Illinois No. 6 (ball mill and ultrasonic), but are not directly comparable because of size differences in the original samples. Histograms plotted for the Upper Freeport samples reveal that the size range of the ball mill particle population is much smaller (350-1, 800,000 cu. μ) than the ultrasonic population (350-4, 800,000 cu. μ). This leads to a mean particle volume of 22,493 cu. μ (S.O. = 86,048) for the ball mill sample as opposed to a mean of 137,321 cu. μ (S.D. = 405,442) for the ultrasonically ground sample. The percentage of sample, by weight, in the smaller size ranges was also compared for the two grinding processes. The size distribution of the ball-mill-ground sample is clearly shifted toward the finer end of the distribution relative to the ultrasonic distribution. The two Illinois No. 6 samples also show similar trends. Furthermore, these results demonstrate the difference in grindability between the difficult-to-grind Illinois No. 6 and the more easily comminuted Upper Freeport.

Statistical tests based on the analysis of means and standard deviations of width/length measurements indicate that ultrasonic grinding produces particles that are more elongated than does ball mill comminution. This statement holds true when comparing Upper Freeport (ball mill) to Upper Freeport (ultrasonic) and when comparing Illinois No. 6 (ball mill) to Illinois No. 6 (ultrasonic). However, insufficient samples have precluded comparing the two coals and two methods simultaneously.

Also during this reporting period, Upper Freeport (ultrasonic and ball mill) samples were subjectively compared by use of high resolution SEM. There appears to be less bounded (coal-enclosed) mineral matter in the ultrasonically ground coal. In addition, ultrasonically ground coal particles display a higher degree of angularity when contrasted with ball mill samples. Examination of composite particles (coal/mineral) has revealed no preferred fracturing along mineral/coal contacts. (Southern Illinois University)

Preparation of Low-Rank Coal

The overall objective is to develop methodology to prepare stable low-rank coal-water slurries with high enough solids and Btu contents that they can be utilized economically as replacement fuel for oil-fired combustors or as feed to high-pressure gasifiers. A further goal is that these slurries can be transported by pipeline. The key to

accomplishing these objectives is the development of an economical coal-drying procedure that gives a product that is resistant to moisture reabsorption. One of the most promising processes is hot-water drying of finely ground coal in slurry.

Construction of the hot-water coal-drying process development unit was continued. The instrument panel was assembled, and all instruments except one strip-chart recorder were installed. The cable tray layout was finished, electrical service was completed to all low-voltage motors, and work continued on completing the wiring to all high-voltage motors. The two water storage tanks were modified to accept level transmitters and sight glasses, and installation of the vacuum lines to the slurry flash concentrators was completed.

The 14 electrical resistance wire jacket heaters for process equipment heating were installed and insulated, the coal-drying reactor was mounted, and the outlet piping was completed. Work continued on both the electrical and pneumatic instrument control loops, and the 277-volt electrical service to the heaters on the coal-drying reactor was completed. Also, work was started on the construction of the slurry storage tank mezzanine.

The liquefaction continuous process unit was modified, and the piping reconfigured to permit the unit to be used for hot-water coal drying. Approximately 200 pounds of pulverized Indian Head lignite were subsequently hot-water dried at 300°C and 330°C. The resultant coal-water slurry was stable but was dilute at only about 35% dry solids. All of the product slurry was shipped to Brigham-Young University, where it will be concentrated and used in atomization studies.

The slurry rheology studies using hot-water-dried Indian Head lignite were continued, and graphs of apparent viscosity versus solids loadings were constructed. These studies indicate that for coal-water slurries formulated with Indian Head lignite, which has been hot-water-dried at 330°C, bone-dry solids concentrations of 58 wt% are relatively easy to achieve and have a viscosity of about 800 centipoise when measured at 410 reciprocal seconds. By comparison, slurries formulated using "as-received" lignite became non-pourable when the coal content reached 40-wt% bone-dry solids. Conventionally drying the lignite to 14% moisture before slurry formulation only helped slightly. In this case, the slurry became un-pourable when the solids level reached 42 wt%. (University of North Dakota, Energy Research Center)

Expansion of Coal Preparation Plant Simulator

Work is about to begin on the thermal-dryer module. This will be the last major model within the dewatering category. The anticipated completion for this model is early fall. A first attempt to provide overall water-balancing capabilities has been completed. The model appears to be somewhat simplistic, and refinement will continue through the summer. Work is progressing satisfactorily on a "user-friendly" data input routine, which will greatly facilitate the user's data entry task. To simplify the microcomputer implementation, the tabular washer performance data have been replaced by Weibull function approximations. A comparative study of the use of the Weibull function versus the use of the original tabular data will be completed this summer.

A new moisture function that offers more accurate calculations than the former model has been developed. (The moisture function is used to determine the percentage of water associated with a given coal stream as a function of the size distribution of the coal.) This function will be incorporated into the overall simulator structure during the next quarter. A working version of the Fortran compiler for the IBM Personal Computer was obtained. Using this compiler, the 33 separate programs that make up the simulator were compiled and linked. This was accomplished without segmentation of the program, thereby avoiding the associated penalty in execution time. Following debugging, the program successfully executed a typical plant simulation in 15 minutes, a considerable improvement in execution time over the previous Apple II version. This marks a potential increase in performance of the simulator for the industrial user with a personal computer.

A letter stating the current status of the coal preparation plant simulator was written to all of the simulator users. The letter describes the features of the latest mainframe version of the simulator and announces that it will be ready for distribution in the fall. The letter also describes the features of the IBM PC version that will also be available this fall. The letter states the procedure for obtaining a tape or disk copy of the latest version of the simulator when it becomes available. A mailing list containing over 80 current simulator users has been stored on a data base. The mailing list, which will be updated periodically, will be used to distribute this letter and others written in the future to inform the users. (University of Pittsburgh)

ENVIRONMENTAL COORDINATION

E.W. Evans, Cost Account Manager

F.R. Brown, Chief, Environmental Control Technology Project Management Branch

The primary responsibility of the Environmental Coordination Section is the initiation, management, and coordination of those projects relating to the environmentally acceptable development and utilization of fossil energy. Ancillary to this, the Section assesses and comments on the consequence of proposed and existing environmental legislations and regulatory statutes on DOE Fossil Energy activities, and also reviews and evaluates environmental-monitoring plans for those projects seeking financial assistance from the Synthetic Fuels Corporation.

Peat

The objective of the Peat Program is to develop a technology base for peat harvesting and dewatering to ensure the effective utilization of the U.S. peat resource. Special attention will be given to advanced technology development for wet harvesting, dewatering, and environmental acceptability as related to various geographical areas of the country where peat may be used for energy purposes.

Compendium of Information About Peat

A draft report compendium of information about peat has been prepared with the following objectives: (1) identify the risks to be considered in the application of foreign, commercial peat methods in the United States, (2) review the commercial readiness of second-generation peat harvesting and dewatering methods, and (3) identify technical, economic, environmental, and social issues that must be addressed in conjunction with peat use in the United States.

The report emphasizes the areas with the greatest degree of uncertainty with respect to performance, operability, economics, environmental impacts, and commercialization risks. A final report on the study is expected in July 1984. (Peat Systems International)

Physicochemical Characterization of Peat

The objective of this project is to (1) predict the optimum composition properties of a peat that will produce the best wet-carbonization characteristics, (2) suggest modifications in plant design or reaction temperatures necessary to accommodate the variability of the peat in a particular area, and (3) establish a means for blending peats

to achieve feedstock characteristics for a specific process (or plant design).

The purpose of these undertakings will be to determine the effects of physicochemical variations in peat composition upon wet carbonization and dewatering properties. The work plan for accomplishing this goal has been broken up into six basic tasks:

- Task 1. Sample collection
- Task 2. Petrographical/Botanical Analyses
- Task 3. Chemical Properties
- Task 4. Physical Properties
- Task 5. Wet-Carbonization Characteristics
- Task 6. Data Analysis and Project Management

This quarter, four peat samples of about 250 pounds each were collected from well-known peat deposits in the United States. Three of these samples were from Minnesota and one from Maine. Splits of the four samples have been sent to the Institute of Gas Technology, where wet-carbonization and dewatering tests have been started. Initial preparation has also begun for petrographic and geochemical analyses at Los Alamos. (Los Alamos National Laboratory)

Development and Testing of a Novel Mechanical Device for Dewatering Peat

The objective of this program is to develop and test a novel mechanical device for dewatering peat. This Internal Rotary Compression press (IRC) is a compact field-portable unit that is capable of delivering simultaneous high compression and shear forces to dewater peat.

The program is divided into two phases. The first phase is to validate the concept. A laboratory-scale unit will be designed, fabricated, and tested under several operating conditions. If the results from Phase I are favorable, a prototype IRC will be designed, constructed, and tested in Phase II to obtain process and operating data for performance, engineering, and economic evaluation.

Phase I of the development of a novel IRC was completed. The validation-of-concept of the IRC was successfully carried out by Institute of Gas Technology (IGT). Laboratory tests showed that raw Minnesota peat can be dewatered from 90% to less than 50% moisture by using an IRC press.

Plans for Phase II were reviewed and approved by DOE and the Minnesota Department of Natural Resources. The Phase II work on the design and construction of a prototype IRC system for studying the effect of operating variables on product quality and yield of dewatered peat will begin in June 1984. (Institute of Gas Technology)

Experimental Program for the Development of an Advanced Wet-Carbonization Process

The objective of this contract is to conduct an experimental program to obtain data to facilitate the development and optimization of an advanced process for wet carbonization of peat. Wet carbonization is a beneficiation process to produce a product that can be dewatered mechanically to low moisture contents (about 30 wt%) and that has up to 33% higher heating value (on a dry basis).

The program is divided into three major tasks. In task 1, tests using an existing Process Research Unit (PRU) will be conducted to determine the wet-carbonization characteristics of peat under various operating conditions. In task 2, energy and chemical recoveries from process liquid effluent streams will be evaluated. In task 3, using the results from the previous two tasks, process engineering and economic studies will be conducted to identify the optimum set of operating conditions for wet carbonization.

Task 1 - Process Research Unit Tests

During this quarter, six successful PRU tests were completed. Four of six tests were voluntarily terminated after two hours of steady-state operation had been achieved. A heat loss study using water feed was also conducted for steam injection and reactor systems.

Three tests were short-residence-time tests in which a 9-wt% slurry was heated by steam injection, fed to a one-gallon reactor, and rapidly cooled. Nominal operating conditions for these tests were 400°F, 450 psia, and 1-minute residence time, and 500°F, 850 psia, and 1-minute residence time, respectively.

One other test was performed using the 4 reactors and the flash cooling and heating system. Nominal reactor conditions were 350°F, 400 psia, and 40-minute residence time (10 minutes in each reactor). Samples from these tests were sent for analysis and dewatering tests. Additional samples were sent to Bemidji State University for their characterization. Data analyses of previous tests with the PRU and batch autoclave unit continued during this quarter.

Preliminary testing of a centrifuge to be used in the PRU wet carbonization filtrate recycle test was begun.

Task 2 - Product Water Processing

The design and construction of the oxidation pond reactor continued. Overall, construction of this unit is 90% completed. Only a few minor fittings must be installed before the unit is operational.

The two-phase digestion system was operated at a combined hydraulic retention time of 7 days on the filtrate from the wet-carbonization tests. Preliminary non-steady-state data showed a methane yield of 4.4 scf/lb volatile solids (VS) added compared to an ultimate methane yield of 4.8 scf/lb VS added. The COD removal efficiency across the system was 58%, while the BOD removal efficiency of 72% was achieved. Steady-state data will be collected during the next quarter.

Task 3 - Process Engineering and Economics

Material balance data and related information from PRU tests were transmitted to Kellogg Rust Synfuels, Inc., and evaluation of the data has begun. (Institute of Gas Technology)

Critical Points in the Coal Fuel Cycle: A Modeling Analysis

Two tasks are associated with the overall objective of determining the feasibility of using coal models to analyze the coal fuel cycle: (1) the evaluation of existing models, and (2) the selection of a model to be used by the Coal Technology Laboratory at Southern Illinois University at Carbondale (SIU-C). An ancillary objective is the identification and gathering of data pertinent to the coal model in the areas of coal supply and demand, transportation technology and costs, pollution control regulations and the options available to comply with regulations, the costs of these options, and the range of evaluations of sulfur reduction strategies by commercial user and developers.

During this quarter, the Coal Supply and Transportation Model obtained from the Energy Information Administration was placed in operation at SIU-C. The first run of the model was used to compare 1982 coal production with 1985 production as predicted by the model, with no major changes in factors that might influence production, such as new environmental legislation. Three research questions were designed for testing the utility of the model. These questions

were related to the following: (1) proposed acid rain legislation, (2) the use of blended coal to comply with air emission standards, and (3) the development of competitive rail systems for transport of coal from the western U.S. to the East. The proposed acid rain legislations examined included the Waxman-Sikorski bill (H.R. 3400) and the Stafford bill (S.768).

The pollution control technology component of the model, which is mainly in the form of a matrix of scrubber costs, has been updated and improved. An energy penalty for using scrubbers has also been added to the model. The model was tested a second time in order to project SO₂ emissions and resulted in predicted 1985 SO₂ emissions of 20-million tons, which compared favorably with the 1980 actual emissions of 20.1-million tons.

In addition to the modeling developments, the project moved forward in gaining insight into the viewpoints held by those in the coal fuel cycle field, namely, by coal preparation plant managers and corporate executives, as well as by electric utility managers. (Southern Illinois University)

Ancillary Activities

An important activity of the Environmental Coordination Section is the formal review and evaluation of Environmental Monitoring Plans (EMPs) and EMP Outlines for U.S. Synthetic Fuels Corporation (SFC) supported projects. As promulgated in Section 131(e) of the Energy Security Act, any recipient of financial assistance from the SFC must develop an EMP in consultation with DOE, as well as other consulting agencies, for the monitoring of environmental and health-related emissions generated during the construction and operation of a synthetic fuels project. Toward this

end, the project sponsor is required to perform both compliance monitoring and, as appropriate, supplement monitoring. In general, compliance monitoring, which is the concern of EPA, includes all monitoring activities necessary in order to comply with federal, state, and local regulatory obligations, i.e., permit requirements. Supplemental monitoring, which is the concern of DOE, refers to the identification and characterization of unregulated substances that may be present at levels of significant health and environmental concern in the project's process streams or wastes.

The SFC mandates that the project sponsor employs a two-stage approach in developing an EMP. During the first stage, the sponsor must prepare an EMP Outline that contains a general description of the monitoring responsibilities associated with the project. The Outline actually becomes part of the financial assistance agreement between the SFC and the project sponsor. During stage two, the sponsor is required to develop an EMP, which is a more detailed description, based on the EMP Outline, of the specific monitoring tasks to be undertaken in connection with the project. The DOE is intimately involved during all stages of the EMP developmental processes. The DOE's involvement is principally that of a technical consultant via the identification of deficiencies in the EMP, and the proposing of improvements in the EMP process and related activities.

During this quarter, the Environmental Coordination Section has reviewed and provided comments and suggestions to FE/HQ on the EMPs and EMP Outlines for the following projects: DOW Syngas Project; Union Oil's Parachute Creek Oil Shale - Phase II; KRW Keystone Gasification Project; and the Signal Northern Peat Project.

AR&TD: UTILIZATION PROJECTS

J.D. Hickerson, Cost Account Manager
F.W. Steffgen, Chief, Advanced Research Contracts Branch

The objective of these studies is the development of a comprehensive technology base to support expanded direct utilization of coal. The research program comprises fundamental research projects relevant to various aspects of direct utilization, including coal preparation and handling, combustion, and emissions abatement.

Coal Properties, Preparation, and Handling **D. Wildman, Coordinator**

The objectives of these projects are to develop fundamental data concerning properties, preparation, handling, and transport of coal-based fuels.

These projects provide pertinent information for several research fields. Coal-gas as well as coal-liquid fuels are examined for potential use in industrial applications.

Feasibility Study on Liquid Coal Preparation and Coal Char Demineralization

After modification of the Battelle short-contact hydrolysis unit to eliminate problems associated with line plugging, additional runs attempted with preoxidized upper Elkhorn seam coal were not successful in providing liquid and char. The strategy to obtain pyrolysis liquid was then analyzed, and three alternative paths were developed to achieve this objective: (1) revise the Battelle reactor from a tube type to fixed bed, (2) use a glass retorting operation, and (3) try a short-contact, 4-ton per hour, auger-type retort.

Revision of the Battelle reactor from the tube type to a fixed bed was successful in providing useful quantities of liquid and char. Alternative number two, use of a glass retort at Great Lakes Research Corporation, was also successful, resulting in both char and liquid products. The problem with the Great Lakes experiments was the limitation of charge to about 3 lb of coal. To overcome these problems in the future, a pyrolysis system with a capacity of 7 lb coal has been ordered and received.

Experiments were then conducted with the char and liquid obtained from Battelle to determine the maximum amount of char that could be mixed into the liquid while retaining the liquid-like flow tendencies. With successive additions, it was learned that the slurry could contain up to 30% char by weight for the Battelle reactor and upper Elkhorn seam coal. In the case of Kentucky No. 9 coal, the slurry was able to contain up to 35% char by weight and retain its liquid character. Observation of the slurries after standing has shown that they are stable.

A Soxhlet extraction apparatus was set up to extract char from slurry liquid product to determine its particle size and evaluate its solubility into liquid. Initial extraction test data indicate that there is significant solubility of char in the pyrolysis liquids.

Samples of both low- and high-ash chars have been submitted for characterization parameters that include ultimate analyses, proximate analyses, ash composition, and petrographic composition.

Samples of both low- and high-ash chars were submitted to the Coal Research Bureau of West

Virginia University for acid-leaching tests. In a parallel effort, heavy liquid separation tests were performed on both low- and high-ash chars. Ash levels were reduced from 1.9% down to 1.4% for the low-ash char and from 11.4% down to 6.2% for the high-ash chars. In still a third technique in a hydraulically countercurrent flotation cell, low-ash char was reduced from 1.9% down to 1.5% at 9.2 pH. (United Coal Company)

A Program of Basic Research on the Preparation and Stability of Coal-Water Slurries

The final report for the first phase of this project has been received and approved. Additional work is under way further examining and relating surface chemistry, surface charge, wettability, and additive adsorption of coal to its previous history of oxidation and beneficiation and to surface analysis of each coal sample. The objective is to further develop the model for coal-water slurry behavior. (Carnegie-Mellon University)

Flow Characteristics of Coal-Based Fuels

In April, shakedown tests were performed on the High Pressure Loop using steam as the transport gas. Formal testing will begin when all the high-temperature instrumentation is received.

In May and June, tests were begun to study the development of secondary flow patterns around bends and elbows for solid-liquid transport. Acrylic beads with specific gravity of 1.3 and size distribution of 85% finer than 75 microns were mixed with water and used in these tests. Visualization of flow patterns around bends and elbows was possible. Secondary flow patterns were observed in a standard 90° elbow. No secondary flow patterns were visible in tests conducted with long-radius bends.

A paper entitled "Flow Characteristics and Handling Properties of Commercial Coal-Water Mixtures" was presented at the Sixth International Symposium on Coal Slurry Combustion and Technology.

Distribution of Inorganics in Low-Rank Coals

The extent of sodium ion-exchange as a function of the pH was determined for Gascoyne high-sodium lignite.

Palynology studies of coals to identify coalified spores have been carried out with Deno's reagent. This treatment to concentrate sporelike materials is more suited to lignites than to subbituminous coals.

The chemical fractionation of Beulah lignite lithotype was completed. Coals, extracts, and residues resulting therefrom were analyzed. Chemical fractionation of Yampa and Najajo coals was started. Beulah and Gascoyne coals were prepared for determination of their carboxyl group content. Carboxyl content and ion-exchange behavior are closely related. (GFPO/UNDERC)

Dense-Phase Powder Characteristics

During this quarter, two samples of Pittsburgh seam coal (float 1.3 and float 1.5) were pulverized in our coal-processing unit. The samples were classified into various size ranges using a jet sieve.

Shear stress as a function of displacement at various normal loads was measured for the as-received samples as well as fines samples (particle size <43 microns). From these data, the peak shear strength and ultimate shear strength of the samples were determined. It is noted that the peak as well as the ultimate strengths of the as-received samples is reduced by about 35% for both Pittsburgh seam coal samples and by about 17.5% for Illinois coal samples when samples are finely ground to particle size less than 43 microns. It seems the fines in the samples provide a sort of lubricating effect. Shear tests with various blends of powders will be of interest to understand the mechanism of flow and the part played by the fines. Other mechanical properties of these powders were also measured. These results will be discussed in the next report. (U.S. DOE/Pittsburgh Energy Technology Center)

Thermal Decomposition

J.D. Hickerson, Coordinator

The objective of these studies is to develop an improved fundamental understanding of the vaporization of CWM sprays and the thermal decomposition of coal particles in a high-temperature, high-heating-rate environment characteristic of the combustion process. Topics of interest include vaporization of volatile matter, and the formation of char from coal.

Vaporization and Devolatilization of Coal-Water Sprays

The Parker-Hannifin counter-swirl atomizer was studied by high-speed movies at frame rates from 1000 to 10,000 frames/sec. The field of view included the atomizer tip and the first 13 cm (5 in.) downstream. Studies of water and slurry sprays

were made at two different conditions. The fuel mass flow rate was maintained constant at 500 lb/hr, but the atomizing air pressure was varied from 50 psig to 170 psig. Previous still photographs of the Coen atomizer had suggested the presence of pulsations in water sprays. Although all the water and slurry sprays from the Parker-Hannifin atomizer appeared steady to the eye, the high-speed movies showed that each type of spray had pulsations or fluctuations at frequencies on the order of 50 to 200 Hz.

The spray angle also varied as a function of the different atomizing air pressures and of the pulsations in the spray. At 50-psig atomizing air pressure, the water spray angle was as large as 70°. Increasing the air pressure to 170 psig reduced the maximum water spray angle to 55° to 60°, and occasionally spray angles as small as 10° were observed.

Spray velocities were estimated by identifying a group of spray particles/droplets and counting the frames required for this group of droplets to move from the atomizer exit to the bottom of the movie frame. The measured velocities are thus an average over the first five inches of the spray. Average velocities of 50 to 100 m/s (164 ft/s to 328 ft/s) were observed for the 500 lb/hr water spray with an atomizing air pressure of 175 psig.

Similar values for spray angles, velocity, and pulsation frequency were obtained for coal-water slurry sprays. Spray angles up to 75° were observed in the 500 lb/hr spray at atomizing air pressures of 50 psig. As in the case of water sprays, the spray angle narrowed as the atomizing air pressure increased. At atomizing air pressures of 175 psig, the maximum spray angle observed was 50°. The spray angle also varied as a function of the pulsations; minimum spray angles were on the order of 10°.

Spray velocities were approximately 17 m/s (55 ft/s) and 40 to 80 m/s (141 ft/s to 262 ft/s) for the 500 lb/hr slurry spray with atomizing air pressures of 50 psig and 175 psig, respectively. Pulsation techniques were approximately 50 Hz in the slurry sprays at low atomizing air pressures and about 70 to 110 Hz in the sprays at the high atomizing air pressure.

Work is under way to determine the nature and cause of these pulsations. The Hycam II movie camera will be used in this investigation because it has the capability to make simultaneous cine and oscilloscope recordings. In effect, a high-speed movie is recorded with an overlaid streak trace from an oscilloscope, allowing the output of

the pressure transducers on the slurry and air lines to be recorded directly on the film. Using such techniques, it may be possible to trace and identify the source of the spray fluctuations. (Carnegie-Mellon University)

Coal Devolatilization

During this period, a simulator called Dischain, based on free-radical chain chemistry, was formulated and evaluated against an extensive experimental study of one bituminous coal. The mechanism used in Dischain is a lumped version of Gavalas' free-radical pyrolysis scheme that exploits the disparate concentration scales in this complex chemical mix. Only six traction steps survived this simmering: bridge cleavage, peripheral group elimination, heavy radical attack on bridges, heavy radical stabilization, heavy radical condensation to char, and scission of aromatics to oils and gas. A uniform distribution of activation energies represents the very broad range of bridge strengths in the first reaction. The model features a rudimentary parameterization for different coal types and predicts the yields of tar, gases, and char. The polymeric nature of coal is also retained, albeit approximately, from an expression for the evolution of the fragment size distribution as a function of the instantaneous bridge concentration. Few monomers are generated when bridge cleavage begins, but this selectivity for monomers accelerates tremendously as the process proceeds.

The evaluation has already superseded the performance of more than twenty schemes taken from the literature, although the effects of heating rate are not adequately represented during the earliest stages of reaction. An additional step at high temperatures will be evaluated in the coming months, and the predictions will be tested against the results of a recent study of pyrolysis yields from seven coals under conditions of rapid heating.

Fabrication of the new multi-element flat flame burner is nearing completion. The new burner design should improve the sensitivity of the FT-IR technique to minor gas-phase species by increasing the particle loading density and by making the best use of the infrared probe beam shape.

The present burner and flow reactor have been used to quantitatively calibrate the FT-IR system for carbon dioxide at elevated temperatures by seeding either the hydrogen fuel or air with known amounts and measuring the resulting absorbance. This work is continuing with measurements on carbon monoxide, sulfur dioxide and

nitrogen oxides. These calibrations will greatly improve concentration determinations of gas-phase species. Because the FT-IR instrument line-shape function is substantially wider than the actual molecular line shapes, the accurate determination of concentration for these species will depend critically on these results.

Experimental data on coal devolatilization rates can be difficult to interpret because there are many interacting factors influencing these rates. A computer model has therefore been developed to determine the relative importance of such factors as heat conduction and convection to the particle, radiative heat transfer, combustion of the volatiles in the boundary layer, and simultaneous heterogeneous combustion upon the time-temperature history experienced by the particle. Some initial results from this model show that heterogeneous combustion reaches its peak rate at the end of devolatilization due to the high particle temperature caused by oxidation of the volatiles in the boundary layer. This result was previously unknown because it was assumed that the volatiles consumed all the oxygen in the boundary layer. This is a significant finding since higher heating rates cause more of the coal to devolatilize as tar, which in turn affects the quantity of soot formed and the residence time required for particle burnout. (Sandia National Laboratory)

Combustion Kinetics

H. Ritz, Coordinator

The objective of these studies is to develop an improved understanding of ignition and combustion of the products of thermal decomposition of coal. Topics of interest include ignition and combustion of volatiles, and the ignition and combustion of char particles.

Combustion Characterization of Coals for Industrial Applications

Experimental work on this project is complete. Some data reduction and analysis remain to be done. Upon completion of data analysis, the final report will be prepared and submitted for approval.

Combustion Characteristics of Cleaned and Micronized Coals

Previous problems in maintaining combustion of CWM without natural gas were traced to low firing rates (1.5 lb CWM/min). Consequently, four cooling coils were installed in the furnace to permit higher firing rates. Inadequate secondary air

preheat was also suspected, so the controls were modified to permit 550°F preheat. A new carbide-lined burner nozzle was purchased and installed.

Cold spray tests of the old and new burner nozzles were conducted, revealing inadequate atomization by the old burner nozzle at CWM flow of 1.5 lb/min and a realistic atomization air/slurry ratio of 0.53. The new nozzle was satisfactory.

Combustion tests of the old and new burner nozzles, which were both water-cooled, revealed persistent plugging problems, apparently due to tip heating causing the evaporation of some of the water from the CWM before it could be atomized. Measures to correct this are being evaluated, especially the use of a high-thermal-conductivity alloy for the nozzle body and tip, and use of soft metal gaskets to minimize thermal contact resistance. The combustion tests also revealed that the secondary air blower had marginal head for the high-swirl air register, although it was usable at a CWM flow of 1.5 lb/min.

The computer program to evaluate air register designs was modified to handle curved vanes rather than flat vanes. This had a drastic effect on calculated swirl number. The results will be checked by a different (and more complicated) curved-vane model. (PETC)

Fundamental Studies of Low-Rank Coal Combustion

The bench-scale combustion system is now fully operational. Temperatures within the reaction zone of up to 1640°C have been achieved. The three-color optical pyrometer has been used to determine surface temperature. Initial experiments examining the global kinetics of petroleum coke are now under way. Reaction rates for various O₂ concentrations, ranging from enriched 30% to depleted 5% O₂, are being considered. These values are being compared to literature values to verify the performance of this system. (GFPO/UNDERC)

Combustion Characteristics of Low-Rank CWMs

Two coal-water slurries, previously hot-water treated at 300°C and 330°C, have been characterized with respect to solids loading, tendency toward sedimentation, and coal particle size distribution. The raw Indian Head lignite from which these slurries were prepared has also been characterized independently. The ceramic interior for the laboratory combustion reactor has been cast and incorporated into the partly assembled combustion device. (GFPO/UNDERC)

Coal Char Combustion

The recently developed particle-sizing pyrometry system has been used to measure the size, temperature, and velocity of fuel particles burning in hot, oxidizing gas environments. Analyses of data taken with spherical graphite particles (Sphero carb) indicate the need to consider thermal inertia effects when describing the heat transfer characteristics of the particles flowing within the first 25 cm of the reactor. The thermal inertia of the particles prevents them from reaching a state of thermal equilibrium with the gas as they encounter the steep gas temperature gradients near the reactor inlet.

Parameters that describe the overall particle burning rate are determined by using the measurements in a theoretical model of the one-dimensional laboratory reactor. The model allows for mass loss due to reaction, thermal inertia, and convective and radiative heat losses, and the drag forces acting on the spherical particles. Account is made for the hydrodynamic boundary layers formed along the reactor walls. Inputs to the model consist of the properties of the gas environment (oxygen level, and temperature and velocity profiles along the reactor center line) and the inlet particle conditions (apparent density, temperature, velocity, and particle-size distribution). Parameters describing the gas velocity profile are determined from the measured particle size—velocity correlation using the Stoke's flow relation. The unknowns in the model are the kinetic parameters that describe the overall particle burning rate per unit external surface area. Proper selection of these parameters yields calculated particle temperatures that agree with the measured values for all particle sizes.

To date, measurements have been obtained for two coal types burning in gas environments having from 1 mol% to 6 mol% oxygen in the temperature range 1400K to 1500K. Analyses of the data indicate that the lignite particles employed (PSOC-085) are quite reactive and burn at their maximum, diffusion-limited rate. Analysis of data obtained for a hvc-bituminous coal (PSOC-287) is incomplete, but the low temperatures suggest that the intrinsic chemical reactivity of the particle material influences its overall burning rate. Kinetic parameters are being obtained for this coal type. (Sandia National Laboratory)

Coal Heat Treatment

Work was initiated to study the effect of rapid heat treatment on the reactivity of coal chars formed in flames. The method will be to use an ex-

isting high-intensity combustor in which combustion is staged, and to investigate the consequence of delaying the moment of secondary air addition. The effect of the delay will be to heat-treat the char formed in the fuel-rich primary combustion by periods up to 100 msec before the secondary combustion is started. There is reason to believe that this period of heat treatment will significantly affect the "intrinsic" reactivity of the flame-formed char, with a possible reduction in reactivity by as much as an order of magnitude. The practical significance of such a result lies in the potential for improving the design of burners or entrained gasifiers to obtain more compact flames and/or higher reaction intensities. This would be of value, for example, in coal retrofits of oil-fired packaged boilers. (Ohio State University)

Emissions Formation and Reduction

R. Walker, Coordinator

The objectives are to understand the mechanisms for formation of unwanted emissions in pulverized coal combustion and to reduce these emissions.

Investigation of the Effectiveness of Calcium-Treated Coals in the Capture of Sulfur Gases Generated in Staged Fired Combustors

The final report is being assembled for this project and will be completed in July.

Test data have been reported in the AR&TD Contractor meeting held in Pittsburgh, Pa., June 5-7, 1984. (Energy and Environmental Engineering, Inc.)

Fuel-Staging NO_x Control Test Program

All work under the contract has been completed. The final report is essentially completed and will be sent to DOE in the near future for review. A presentation of the results of this work was given at the June Contractors' meeting in Pittsburgh. (Acruex)

Mineral Matter/Ash Behavior

M.P. Mathur, Coordinator

The overall objective of this work is to examine and evaluate various coals and ash levels and to predict their behavior in relation to measurable furnace performance factors. An improved understanding of the transformation of inorganic species during coal particle combustion will be developed. Ash fouling characteristics of low-rank coals and slagging behavior of eastern

bituminous coal containing pyrite will also be examined.

Fundamental Properties Characterizing Coal Minerals and Fireside Deposits

A program was conducted to measure fundamental properties characterizing coal minerals and fireside deposits for pulverized sub-bituminous coal at pilot scale with soot blowing. Ion exchange techniques were applied to modify a subbituminous coal and gain insight into the role of "active ions" that are widely thought to produce deposition problems. The draft of the final report was approved and the final report is being printed. (Babcock and Wilcox)

Pyrite as a Contributor to Slagging in Eastern Bituminous Coals

A project was continued to correlate fouling and slagging in a pulverized-coal furnace with ash chemistry and petrology. Combustion tests were completed on Illinois No. 5 and Lower Kittanning bituminous coals burned in an upward-fired furnace at 100-lb coal/hr feed rate. (Foster Wheeler Development Corporation)

Ash Deposition from Micronized Low Rank Coals

The onset of ash particle agglomerations has been monitored by bench-scale shrinkage and electrical resistance measurements on several coal ashes. Ash fouling in pilot-plant operation corresponded quite well to the early onset and extent of ash shrinkage with increasing temperature. The electrical resistance measurements did not provide as good a correlation but generally showed increased conductivity at lower temperatures for coals given to ash fouling. (GFPO/UNDERC)

Ash Fouling by Low-Rank Coals

The first draft of the Topical Report is over 90% complete. Scheduled completion of this report is September, 1984. (GFPO/UNDERC)

Fate of Mineral Matter During Coal Combustion

Samples have been prepared for calibration of the automated SEM and microprobe systems. These samples contain varying proportions of quartz, pyrite, and several different clays and will be used to determine the precise calibration factors that need to be used in interpreting the results of the automated analysis. Previous work using this automation software has relied upon calibrating factors published by the software sup-

pliers. The use of in-house measured factors should improve the accuracy of this form of analysis. The calibrations will be carried out in the next quarter.

Work has begun on a set of five coal samples obtained from researchers at the National Bureau of Standards. The samples were provided for analysis in our SEM instrument. The samples were obtained from the same specimen of ground coal but were subsequently tested in a differential scanning calorimeter at NBS and gave differing results. This laboratory was contacted to detect differences in the samples that could be correlated with the varying differential scanning calorimetry data.

The final manuscript for the low temperature ash report was finished this month, and the report

was published. A shortened version of this report will be prepared and submitted to Fuel. (Sandia National Laboratory)

*A Study of Mineral Matter Distribution
in Pulverized Coal with Respect to Slag Deposit
Formation in Boiler Furnaces*

The draft final report was reviewed and a few necessary changes in format are under discussion. (Pennsylvania State University)

*Mechanisms of Fouling, Slagging, and Corrosion
by Pulverized Coal Combustion*

The final report for this project has been received. (Solar Turbines)

AR&TD: LIQUEFACTION PROJECTS

G.V. McGurl, Cost Account Manager

F.W. Steffgen, Chief, Advanced Research Contracts Branch

The objectives of the AR&TD liquefaction program are to develop a technology base for coal liquefaction through research on the basic principles involved and to explore new and improved process concepts for both direct and indirect liquefaction. The first activity will provide a knowledge base to facilitate transfer of the technology to private industry at an appropriate time. The second objective provides early evaluation of new concepts to determine if they offer enough promise to continue development in the coal liquefaction PR&TD program described elsewhere in this report. To facilitate organization and reporting, the AR&TD program has been divided into four subcategories: Exploratory Research, Indirect Liquefaction, Catalysis and Kinetics, and Coal Science.

Exploratory Research

G.V. McGurl, Coordinator

A series of 24 nickel and palladium titanate catalysts was prepared from tetraisopropyl titanate by conversion to a sodium or potassium hydrous titanate intermediate and then ion-exchange with aqueous $\text{Ni} + 2$ or $\text{Pd} + 2$ solutions. The nickel catalysts contained from 5 wt% to 10 wt% Ni; and the palladium catalysts, from 10 wt% to 17 wt% Pd. Acidity of these catalysts was modified by contact with solutions of tetramethyl ammonium hydroxide or phosphoric acid. Cata-

lysts contacted with the base absorbed 0.4 to 0.8 meq./gm of hydroxide while those contacted with acid absorbed 1.3 to 3.0 meq./gm hydrogen ion. (Sandia National Laboratories)

Synthesis rate expressions were developed for four different iron catalysts: iron carbide, iron oxide, potassium-promoted iron oxide, and potassium-promoted fused iron. Data for each of these catalysts can be correlated by a semi-empirical expression: $R_{C_n}/\alpha^n = K P_{H_2} P_{CO}^{0.5}$, where R_{C_n} is the rate of synthesis of a product containing n carbon atoms, and α is the probability of chain growth. For the two promoted catalysts, α is virtually independent of P_{H_2} , P_{CO} , and T , and hence the equation provides the overall dependence of the rate for each product on P_{CO} and P_{H_2} . For the unpromoted catalysts, α is a complex function of P_{H_2} and P_{CO} and T . Since R_{C_n} is proportional to α^n , this explains the chaining dependence of R_{C_n} on P_{H_2} and P_{CO} with n observed for these unpromoted catalysts. (Lawrence Berkeley Laboratory)

Solubilization of a Marylee seam coal from north of Birmingham, Ala., in the liquid clathrate $K[\text{Al}_2\text{Me}_6\text{N}_3] \cdot 4$ toluene at room temperature was investigated. Approximately 25% of the coal was converted to liquids. An analysis of the liquids by GC/MS showed a large number of compounds, none of which was dominant. (University of Alabama)

Reaction of benzylphenyl ether with the Lewis acids $\text{CF}_3\text{SO}_3\text{H}$, BF_3 , $\text{BF}_3 \cdot \text{CH}_3\text{OH}$, and AlBr_3 in benzene solutions was investigated at room temperature. Analysis of the products showed that in each experiment approximately one half of the ether converted to diphenylmethane, and one half to o-benzylphenol. While the former is a product of the cleavage of the ether linkage by an intermolecular process, the latter is clearly a product of intramolecular rearrangement. Similar results were also obtained with 1-naphthylmethylphenyl ether and BF_3 , although with this ether the products contained significant quantities of the rearranged p-phenol in addition to the o-phenol. These observations are of significance to the chemistry of coal liquefaction in that the cleavage of ether bonds is believed to be one of the principal mechanisms in depolymerization of coal. (Iowa State University)

A Bakerstown coal, powdered to 150/200 mesh, was extracted with blends of tetralin (4 parts) and tetramethylurea, ethylenediamine, quinoline, or dimethylacetamide (1 part) at atmospheric pressure and at 200°F to 300°F. The blend of tetralin and dimethylacetamide was the most effective solvent. On an ash-free basis, about 21% of the coal was extracted with this solvent. (Montana State University)

A stainless steel reactor cell designed to permit in situ X-ray absorption spectroscopy of three-phase catalytic reactions at temperatures up to 700K and pressures up to 14 MPa was constructed. The X-ray beam enters and leaves the cell through thin (0.051 cm) beryllium windows. The design of the cell is such that heat transfer from the reaction chamber to the windows is minimal. When the cell was operated at 520K, the windows were near room temperature. Because of this feature, the beryllium windows can withstand repeated cycling to high pressures in corrosive environments. (Stanford University)

An analysis of the kinetics of solvent mediated hydrogenolysis reactions of model compounds and coals indicates that the critical cleavages in coal liquefaction are a result of hydrogen transfer, not the cause of it. Coals promote cleavage of bonds that are too strong to undergo thermal scission under liquefaction conditions. The 1-hydronaphthyl radical is the active H-transfer agent by a bimolecular process. The rate of a solvent-mediated hydrogenolysis reaction markedly increased when the proportion of hydronaphthyl radicals was increased. (SRI International)

The polar components of coal liquefaction solvents have been isolated using activated ion-

exchange resins. The OH-concentrate of SRC-II contains primarily one- and two-ring phenolic compounds consisting of phenol (~4%), methyl phenols (~9%), C_2 to C_5 phenols (9%), and indanols (~8%). Only 0.4% are naphthols. The total aromaticity of this fraction is about 77%. The aliphatic groups consist of methyl groups (26% of the H), long-chain alkyls (average of five carbons at 17% of the H), and a fairly substantial level of hydroaromatics (6% of the H). There is also present a nominal level (1%) of methylene bridges between rings. The SRC-II N-concentrate has about an equivalent aromaticity at 72%, and its nominal ring size is between 1 and 2. It contains both nitrogen and hydroxyl functionality (but apparently not on the same ring). The alkyl groups are divided among methyl groups (20%), long-chain alkyls (average of three carbons at 23% of the H), and a high level of hydroaromatics (12%). Anthracene oil, which is derived as a coke oven by-product, has an N-concentrate with a high level of aromaticity (95%) and an apparent ring size of 1 to 2. The N-concentrate again contains both nitrogen and hydroxyl functionality. The aliphatic carbon is divided among methyl groups (16% of the H), short-chain aliphatics (1.4%), and a low level of hydroaromatics (2.1%). (Gulf Research & Development Co.)

Indirect Liquefaction

R.R. Schehl, Coordinator

The objectives of the research conducted within this category are directed at developing a better fundamental understanding of the chemical and physical processes associated with the catalytic conversion of coal-derived synthesis gas to liquid fuels. Emphasis is placed on characterization and testing of new catalyst formulations to provide insight into the mechanisms involving catalyst activity, stability, and selectivity. Another objective is to establish a quantitative understanding of mass transfer related factors that determine reaction rate and selectivity in three-phase liquefaction reactors.

Addition of H_2S to synthesis gas with catalyst suspended in octacosane increased catalyst activity by 60% at a sulfur loading of 1.3 mg S/g Fe, beyond which catalyst activity decreased. The H_2S had little effect on molecular weight distribution or on such secondary reactions as olefin hydrogenation and olefin isomerization, or on oxygenate concentration. Dibenzothiophene, present in phenanthrene during start-up, markedly decreased catalyst activity. It also caused a marked drop in selectivity to form methane, a reduc-

tion in secondary olefin hydrogenation, and an increase in secondary olefin isomerization, but it had no effect on oxygenate concentrations. (Massachusetts Institute of Technology)

Using ^{17}O exchange between the faujasite of interest and ^{17}O enriched water, ^{17}O enriched faujasites of different framework Si/Al ratio can be successfully prepared for ^{17}O NMR studies. As a result, commercially available faujasites can be easily ^{17}O enriched in the NH_4^+ form for ^{17}O NMR characterization. The use of ^{17}O MASS or VASS NMR greatly narrows the ^{17}O NMR static line, allowing chemical-shift results to be obtained. In the next quarter, the main effort of this program will be directed toward obtaining ^{17}O NMR results on faujasites of various Si/Al ratios to examine the dependence of the ^{17}O NMR properties on Si/Al ratio and cation type. (UOP, Inc.)

A number of unsteady-state FT synthesis experiments were conducted in a vibrofluidized-bed microreactor wherein low H_2 :CO synthesis gas and pure H_2 fluidizing gas were alternately pulsed through the reactor. The synthesis gas feed was set at a flow rate equivalent to one reaction zone volume in 2 seconds, while the fluidizing gas feed flow rate was equal to one reaction zone volume in 5.3 seconds. The results showed that carbon deposition could not be prevented under these gas-cycling conditions: 1.01 gm of catalyst charge had gained a net weight of 0.2818 gm. (VPI and State University)

Catalysis and Kinetics

H.R. Appell, Coordinator

The objectives are to (1) study kinetics, mechanism, and catalysis of coal liquefaction and heteroatom removal, (2) conduct research leading to the development of inexpensive disposable-type catalysts or new long-lived catalysts for coal liquefaction, hydrodesulfurization, and hydrodenitrogenation, and to gain an understanding of the mode of their effectiveness, and (3) conduct liquefaction studies in support of potential larger-scale processes.

The BET surface area of unsupported molybdenum sulfide was found to be dependent on details of preparation and pretreatment. Using mild conditions for removing some of the sulfur in MoS_x ($x = 2.2\text{--}2.3$), such as reduction in hydrogen at 250°C , essentially none of the surface area, 39 m^2/g , of a product obtained by flash decomposition of ammonium thiomolybdate in helium was lost. Reduction in hydrogen at 450°C , however, resulted in a loss in surface area to 16 m^2/g to 17

m^2/g . If hydrogen sulfide was present during the reduction at 450°C , no surface area was lost. The data suggest that sintering occurs at some critical value of anion vacancy concentration. The unreduced sulfide showed negligible catalytic behavior for the hydrogenation of propylene at 100°C . After reduction at 250°C , some catalytic activity developed with no change in the surface area. When the reduction was carried out at 450°C , there was a large increase in the catalytic activity, although the surface area was reduced to half of its original value. (SUNY at Buffalo)

Sulfided cobalt and nickel molybdates, both on alumina, were compared for hydrotreating anisole. The cobalt catalyst gave conversions of 0.5%, 1.5%, and 65.6% at 170°C , 260°C , and 350°C , respectively. Phenol was the major product at all temperatures. The nickel catalyst showed similar behavior under 200°C , but its activity increased more rapidly with temperature. At 320°C , an 81.5% conversion was obtained, with phenol again the main product. Both catalysts formed o-cresol as the major by-product. The cobalt catalyst formed a few percent of 2,4,6-trimethylphenol at 350°C as a minor by-product, whereas the nickel catalyst formed 2,6-dimethylphenol at 320°C as a minor by-product. (University of Utah)

The effect of adding trifluoroacetic acid, a Bronsted acid, on the catalytic hydrodenitrogenation of SRC-II with sulfided CoMo was investigated at 400°C , 1200 psig, and a residence time of one hour. In the absence of any additive, the sulfided CoMo reduced the nitrogen content of the feedstock from 0.92% to 0.75%. When trifluoroacetic acid in the amount of 4 wt% was added to the reaction, the nitrogen in the SRC-II product was reduced to 0.64%. Doubling the acid addition resulted in a further decrease in nitrogen to 0.53%. Analysis of the liquid and gaseous products showed that at least some of the trifluoroacetic acid had decomposed during the hydrotreating reaction. The catalyst showed a 0.14% fluorine content, and the gaseous effluent showed the presence of trifluoromethane. (SRI International)

Studies have been started on a composite bed catalyst system in which different temperatures and/or catalysts are used in specific zones of hydrotreating reactors to improve upgrading efficiency. Preliminary results show increased metals pickup by the catalyst in the hotter zones of the reactor, and that within individual catalyst particles, the metals had a tendency to accumulate near the surface. During the course of the 72-hour test periods, the hydrogen content of the product decreased only slightly, but the nitro-

gen content increased from near 0.2% to near 0.4%. The nitrogen content remained lower throughout the test where 20% of the bed (inlet) was held at 450°C compared to an isothermal test at 400°C. (Oklahoma State University)

The hydrodenitrogenations of carbazole and N-ethylcarbazole were compared at 320°C, 2500 psig, and sulfided cobalt molybdate. Both compounds formed the corresponding 1,2,3,4-tetrahydro derivative, which then split out ammonia as it was converted to dicyclohexyl as the major product with lesser quantities of hexylcyclohexane and cyclohexylcyclopentane. Tests with pure dicyclohexyl showed no evidence for the formation of hexylcyclohexane and cyclohexylcyclopentane, suggesting that these two compounds were derived from the tetrahydro derivative or other intermediate but not the dicyclohexyl. Determination of the reaction rate constants showed that carbazole was hydrogenated more rapidly than its N-ethyl derivative, most likely because of the steric effect of the ethyl group in preventing flatwise adsorption of the benzene rings. The reaction rate constants for the formation of the nitrogen-free products were larger for the N-ethylcarbazole than for carbazole because of the ethyl group's influence in weakening the C-N bond. (University of Utah)

Coal Science

M. Perry, Coordinator

The objectives include the characterization of fundamental structural and functional units present in fossil fuels and coal conversion process streams. An anticipated enhancement of data retrieval and utilization will accrue through the creation of a coal sample/data bank to facilitate future investigations of coal conversion processes.

Curie-point pyrolysis mass spectrometry of fresh and weathered Hiawatha coal has shown that weathering decreased the yield of naphthalenic moieties but increased the yield of aliphatic carboxylic and carbonylic moieties. These findings are in agreement with the classical views of coal weathering as a process characterized by the formation of ether bridges between aromatic nuclei with a concurrent reduction in free phenolic hydroxyl groups and the oxidation of aliphatic moieties to carbonylic and carboxylic functional groups. (University of Utah)

The development of dependable, accurate instrumental methods for the total accounting of the sulfur balance in representative samples of synfuel process streams (using calorimetric and electroanalytical techniques) is in progress.

These will include determinations of polysulfides, dithionates, and polythionates. Two aqueous samples from different stages of the Lummus Process have been analyzed. As expected, total sulfur content was low. The pH of an aqueous supernatant of a coal-recycle oil slurry sampled prior to liquefaction by the Lummus Process was 5.9. This compares with a pH of 6.2 of a post-liquefaction aqueous effluent obtained from the Wilsonville H-Coal plant and subsequently treated at PETC, where sulfide and ammonia were removed. The similar acidity of the two specimens sampled from entirely different process streams is accounted for by the presence of phenol as the pH-controlling agent in both. (Pennsylvania State University)

Oxygen contents of 21 Kentucky and 14 Penn State Data Bank (PSOC) coals have been determined by gas neutron activation analysis (FNAA). All analyses were done with freeze-dried coals. Oxygen contents of low temperature ashes and acid-demineralized samples from the PSOC coals were also measured. The FNAA oxygen analyses on acid-demineralized samples yield organic oxygen contents directly, while total oxygen minus low-temperature-ash oxygen by FNAA provides an independent organic oxygen value. A pyrolysis-coulometry method of oxygen determination was also applied to the acid demineralized and whole PSOC coals. All these methods yield results for organic oxygen, which are generally in good agreement. Results by ASTM and Given's oxygen-by-difference methods based on ultimate analyses agree in many, but not all, cases. Several equations were developed to express the correlation between inorganic oxygen and silicon on a freeze-dried, whole coal (wc) basis. The best fits to experimental data were obtained with quadratic and log-log equations. The preliminary quadratic equation developed is the following:

$$(O_{\text{inorg}})_{\text{wc}} = 0.835 + 2.959(\text{Si}_{\text{wc}}) - 0.0654(\text{Si}_{\text{wc}})^2$$

This equation partially compensates for high contents of quartz and/or non-silica oxygen minerals (e.g., carbonates and sulfates), which deviate significantly from clay mineral O/si stoichiometry. Only 3 out of the 35 coal samples analyzed deviated appreciably from the above relationship. The mineralogy of the samples is currently being studied, and a detailed interpretation of the data will be presented later. (University of Kentucky)

Requests for samples and compositional data on the 52 coals that make up the DOE Sample Suite in the Penn State Coal Sample Bank are

continuing to be fulfilled to the coal research community. Samples and data are used to develop an understanding of the relationships of

compositional characteristics, coal particles, and coal behavior in utilization. (Pennsylvania State University)

AR&TD: UNIVERSITY COAL RESEARCH PROJECTS

S. Akhtar, Cost Account Manager

F.W. Steffgen, Chief, Advanced Research Contracts Branch

The Office of Fossil Energy supports a program of fundamental scientific and technical investigation in broad areas of coal research pursuant to Public Laws 95-91 and 98-146. The program is limited to support of university research in such areas as coal science and in innovative, fundamental research pertinent to coal conversion and utilization. The program is also intended to encourage faculty members and their institutions to undertake coal-related research and to provide support for students interested in pursuing a career in coal research.

Coal Science

L.E. Makovsky, Coordinator

The objective of the coal science technical activity is to support basic and applied scientific research on coal, coal-related disciplines, and instrumentation directed toward the analyses of these materials. This activity will provide an improved knowledge base directed toward a scientific understanding of underlying phenomena and will build a scientific data base of fundamental physical and chemical properties. The improved knowledge and data bases can enhance the efficiency, environmental acceptability, and economic competitiveness of direct coal utilization systems.

Preliminary testing of the supercritical fluid extraction/fractionation equipment has been started. Restrictor dimensions necessary for a wide range of flow rates and pressures have been calculated. Operation of the mass spectrometer in the chemical ionization and electron impact modes when coupled to the supercritical fluid chromatograph was investigated. The best performance (low background noise and increased sensitivity for high molecular weight compounds) was obtained under chemical ionization conditions. Construction and preliminary testing of the supersonic jet detection system are well under way. Two vacuum still bottoms samples were also analyzed by supercritical fluid chromatography on an *n*-octylpolysiloxane stationary phase and with fluorescence detection. (Brigham Young University)

Methodology has been developed to analyze sulfur-containing polycyclic aromatic hydrocarbons in coal-derived liquids. This technique uses a calcium/mixed amine reduction scheme in which sulfur-containing PNAs are reduced to an appropriate substituted thiophenol. Negative ion chemical ionization in conjunction with tandem mass spectrometry is then used to identify alkyl thiophenols formed by the reduction treatment. A paper detailing the characterization of sulfur-containing PNAs in a middle distillate of an SRC-II product was recently presented at the 32nd Annual Conference on Mass Spectrometry and Allied Topics in San Antonio, Tex., May 27 to June 1, 1984. (Purdue University)

Dynamic and equilibrium swelling studies for pyridine in seven bituminous and lignitic coals from the Pennsylvania State University Coal Bank were continued. After extraction with pyridine at its boiling point (115.5°C) for three to eight weeks, swelling studies were carried out at 35°C. The results of these experiments were used to calculate the number average molecular weight of the cross-links between coal moieties.

Thermochemical analysis was also carried out to investigate the viscoelastic properties of the above coals. The deformation of a coal under various loads (stresses) was measured as a function of temperature. (Purdue University)

Quantitative solubility measurements of nine model compounds and seven coal-derived preasphaltene samples (four native, three derivatized by acetylation) have been carried out in twelve solvents. Plots of model compound solubility vs. solubility parameter exhibited, in general, maxima of ca. 9 to 9.5 Hildebrands (H), in agreement with literature results for coal-derived asphaltenes. Similar plots for the native preasphaltene samples revealed maxima of ca. 10.5 to 11 H, in accord with reported studies. Little correlation between solubility of model compounds and either net hydrogen-bonding indices or donor number minus acceptor number values of solvents was observed. General trends of increasing dissolvability of preasphaltenes with increasing net hydrogen-bonding indices or increasing donor

number minus acceptor number values of solvents were noted. (University of North Dakota)

Chromatographic fractions of the residue and THF solubles from liquefaction of Wyodak No. 3 coal in tetrahydroquinoline at 785°F under 1100 psi H_2 were analyzed by combined microbore HPLC/FT-IR and field ionization mass spectrometry techniques. Major nitrogen components observed by both techniques were THQ dimer and related compounds and their alkylated products. These results suggest significant adduction of nitrogen-containing compounds to coal-derived fragments occurred. Also, a superior FT/IR flow cell has been developed for combined microbore HPLC column chromatography/FT-IR experimentation. The flow characteristics, and spectrometric and chromatographic performance of this flow cell under typical operating conditions were determined. Detection limits have been established to determine combined microbore HPLC/FT-IR sensitivity. (Virginia Polytechnic and State University)

The effects of natural and laboratory-induced stresses on the optical properties and carbonization behavior of coals are being investigated. The bireflectance ratio of vitrains of different ranks, and the total organic volatiles evolved from them at 250°C were determined. The vitrains of low reflectance ratio gave high yields of total organic volatiles. (West Virginia University)

A technique for laser-induced, time-resolved fluorescence spectrometry is being developed to determine the fluorescing compounds present in coal. The sensitivity of the technique was studied by synthesizing fluorescence pulses of known shape and comparing deduced decay times and preexponential factors with the known values. The agreement was within $\pm 10\%$. These sensitivity checks lend confidence to the technique. (Southern Illinois University)

Cross polarization/magic angle spinning ^{13}C NMR spectra of powdered coals do not have good structural detail, and their signal-to-noise ratio is too low to permit Fourier self-deconvolution. It was therefore decided to investigate the feasibility of using chloroform extracts of coal to determine the concentration of functional groups. A high-volatile B bituminous coal was extracted with chloroform, and the ^{13}C spectrum of the extract, which amounted to 4.1% of the coal, was obtained. The spectrum showed high concentrations of molecules with long polymethylene chains. Resonances due to carbon atoms in aromatic rings and in heterocyclic and vinylic

groups were also observed. (University of California - Riverside)

Researchers at Yale University have developed a unique probe for multiple decoupling experiments. A specially designed electronic circuit within the probe reduces the power consumption required to generate the proton decoupling field by a factor in excess of four. (Yale University)

Surface Science

V.U.S. Rao, Coordinator

The objectives of the research conducted within this category are directed at developing a better fundamental understanding of surface phenomena occurring in gasification and catalytic reactions. The influence of promoters and additives in catalytic synthesis gas reactions will be investigated with the aim of delineating the factors that are responsible for increasing the selectivity to higher alcohols and for enhancing chain growth in hydrocarbon synthesis. The catalytic chemistry of heteroatom (O and N) removal from coal liquids will be studied.

Experiments using labeled barium carbonate ($Ba^{13}CO_3$) have been completed, and they show that the interaction of barium carbonate and carbon is quite different than the interaction of potassium carbonate and carbon. Temperature-programmed reaction shows that barium carbonate is not as active as potassium carbonate for CO_2 gasification. When pure $BaCO_3$ was heated in He, no decomposition occurred until almost 1300K. In carbon dioxide gas, some exchange occurred between the carbonate and the carbon dioxide. When $Ba^{13}CO_3$ and carbon were heated in He, decomposition of the carbonate occurred. When $Ba^{13}CO_3$ and carbon were heated in CO_2 , no significant exchange with the gas-phase CO_2 was observed until after gasification of the carbon black. No low-temperature decomposition peaks were seen. Whereas K_2CO_3 decomposed to yield potassium atoms in the presence of carbon, no evidence of barium atoms was obtained. It appeared that barium oxide formed. The interaction of barium carbonate with carbon does not appear to be as strong as that for potassium carbonate. (University of Colorado)

Extremely rapid nitrogen loss has been observed from $\zeta-Fe_2N$ in H_2 at 523K in both constant velocity Mössbauer and transient mass spectrometer experiments. In order to study the phase change from $\zeta-Fe_2N$ to $\alpha-Fe$ in more detail, the hydrogenation temperature was decreased to

473K, and intermediate samples were quenched in liquid nitrogen to lock in the phase distribution for subsequent Mössbauer study. The spectra show complete conversion to α -Fe at or before 21 minutes at 473K. The intermediate samples show evidence of an extremely sharp gradient; only a very small amount of γ' or ϵ phase is observed. Thus, a moving front model of the phase transformation appears to be appropriate. (Purdue University)

Heats of adsorption of pyridine and phenol on powders of untreated and vacuum-oven-dried coals were determined in a flow microcalorimeter. A 12.5-mL solution of the adsorbate in cyclohexane was pumped at a rate of 100-mL per minute through a bed of about 70 mg of coal, and the exotherm was recorded. With both coals, the exotherms reached peaks in about 100 seconds. The heat of adsorption was much larger on the untreated coal than on the vacuum-oven-dried coal. When pure cyclohexane was pumped through the bed, about half of the absorbed pyridine and phenol desorbed endothermically in 30 minutes. (Lehigh University)

Hydrogenation of CO over Rh/TiO₂ catalysts, unpromoted and promoted with Li, K, and Cs, was investigated in a differential reactor at 300°C, 10 atm, and CO/H₂ = 2. The rate of CO conversion decreased in the order: unpromoted > Li > K > Cs. Although the rates of all the products formed decreased upon alkali promotion, there was significant variation in the rate of formation of various products for the different alkali-promoted catalysts. The variation in activity among the unpromoted and variously promoted catalysts differed by more than a factor of 35 for CO conversion. While the rate of hydrocarbon formation varied by more than a factor of 55, the rate of formation of acetaldehyde and ethanol changed by only a factor of 22, and the rate of methanol formation decreased by only a factor of 4. It appears that alkali promoters have different effects on the formation of oxygenated compounds and that of hydrocarbons. (University of Pittsburgh)

Although some difficulty has occurred in preparing iron boride catalysts, the cobalt preparations produced high surface area cobalt borides. Two unsupported catalysts reduced at 250°C and 350°C, respectively, were tested for carbon monoxide hydrogenation activity and selectivity at 1 atm pressure. The results confirm that boron-promoted cobalt is particularly selective for C₅-C₁₂ hydrocarbons and C₃-C₇ olefins. The methane and C₂-C₄ fractions increase while C₅-C₁₃

fractions decrease with increasing reduction temperature. (Brigham-Young University)

Since carbide phases are formed on fused and supported iron catalysts during Fischer-Tropsch synthesis, an attempt was made to form a surface carbide on iron foil by in-vacuo treatments with ethylene at 250°C to 450°C. The position and width of the C(1s) core level measured by X-ray photoelectron spectroscopy (XPS) were used to characterize the surface carbon. Graphite was rapidly formed at 10⁻⁶ torr of ethylene and at temperatures above 300°C. At 250°C and below, little graphite was formed during exposures up to 72,000 Langmuirs. However, the carbide formed under these conditions appeared to be localized at the surface. Low-pressure carburization fails to produce bulk iron carbide. Procedures known to produce bulk iron carbide can be performed in the pretreatment cell attached to the photoelectron spectrometer in order to synthesize standard samples. This work is in progress. (Northwestern University)

In order to establish fundamental mechanisms applicable to coal gasification, simpler model compounds, namely polymers (resins) of the phenol-formaldehyde family and their non-hydroxylated analogs, are being studied. These compounds possess structural features common to coals, with none of the heterogeneous complexities and natural variabilities. Progress has been made on resin synthesis and characterization and on the design of a gasification reactor to be used in determining the transient kinetics of the chars produced from the model compounds. (Brown University)

A series of dealuminated NaY zeolites was studied by X-ray photoelectron spectroscopy (XPS) in order to determine the changes in surface compositions and chemical states as a result of dealumination. The NaY zeolite was dealuminated using an aqueous solution of H₄EDTA. The XPS data indicated that aluminum and sodium are preferentially removed from the external surface of the zeolite during dealumination. This is presumably due to diffusional limitations of EDTA molecules into the internal cavities of the zeolite particles. It was also found that the Al_{2p} binding energies of NaY are an increasing function of the Al/Si ratio of the zeolite. This illustrates the effects of the Madelung potential on the chemical states of the framework aluminum atoms. The influence of dealumination on the product selectivity in Fischer-Tropsch synthesis over Ru/NaY catalysts is currently being investigated. (University of Pittsburgh)

Reaction Chemistry

S. Friedman, Coordinator

The objectives are to explore the basic reactions that occur in liquefaction of coal, and the phenomena associated with liquefaction, utilizing such techniques as isotopic tracer studies and model compounds research, as well as examination of the role of catalysts in liquefaction and other reactions of coal.

To determine the relative amount of "mobile phase" (small molecules physically entrapped in the coal matrix) present in a coal, a set of "dry" liquefaction experiments (400°C for 30 min) was conducted in the absence of solvent with untreated Illinois No. 6 coal and with Illinois No. 6 coal impregnated with ammonium molybdate. The amount of mobile phase present was examined by measuring the extent of chloroform solubility. The formation of chloroform solubles in the untreated coal (11.5%) was considerably less than that from the catalyst-treated coal (30.7%) and indicated that much of the product resulted from bond cleavage in the macromolecular network rather than diffusional release of a trapped mobile phase. (Pennsylvania State University)

A parametric evaluation of the effect of reaction parameters on the yield of liquids from the combined coal and heavy resid processing has been undertaken. The parameters that have been evaluated are reaction time, reaction temperature, initial hydrogen pressure, and diffusion pathlength of the catalyst. The results show that for the liquefaction of Illinois No. 6 coal in Maya crude, longer reaction times of 60 to 90 minutes and temperatures in the range of 425°C yield more pentane-soluble liquids and less IOM. Higher reaction temperatures promote higher gas yields and higher IOM production. Above an initial hydrogen pressure of 500 psia, the pentane-soluble yield was fairly insensitive to hydrogen pressure. Kinetic studies comparing catalysts with different diffusional pathlengths are now being investigated. Initial results have shown that heterogeneous catalysts used in the hydrotreatment of coal liquids appear to have increased tortuosity factors when compared to fresh catalysts. Decreasing the diffusional pathlength by grinding the extrudates results in increased yields of pentane-soluble liquids from the combined processing. (Auburn University)

The ionic fragmentation of bromobenzene was studied as a function of excitation energy into $^1B_2$ state, with two UV photons being necessary to ionize the neutral molecule. A mass-resolved

analysis revealed a decrease in the $C_6H_5^+/C_6H_5Br^+$ ratio at higher excitation energies, which can be traced to a larger photodissociation cross section for the parent ion. Selected resonant and off-resonant features of the $^1B_2$ state also were excited. Surprisingly, a slightly smaller phenyl/parent ion ratio was observed for a resonant excitation as compared with an off-resonant excitation. An additional ionization pathway through a triplet state is a possible explanation of the observed reduction in the phenyl/parent ratio. (Princeton University)

Since ether linkages are believed to be cleaved in coal liquefaction, the reductive cleavage of di- α -naphthylether is being examined in the presence of potential reductants. Both hydroquinone and mesitol have been found to function as catalysts for the ether cleavage at 450°C. Phenol and 1,3,5-trimethoxybenzene, although not good catalysts individually, do catalyze the ether cleavage effectively when used together. (University of Massachusetts)

Heats of immersion of two quite different sulfonic acid resins, Dowex-50 and Nafion-H, in pyridine were measured at four temperatures between 30°C and 100°C. Over this range, the heat of immersion of Dowex-50 decreased from 17.79 to 17.35 Kcal/H⁺ equivalent, while that of Nafion-H decreased from 19.42 to 17.25 Kcal/H⁺ equivalent. The reason for the greatly different slopes of change in heat capacity is being investigated. (Duke University)

A series of 26 iron oxide catalysts was prepared from ferric nitrate and a variety of support materials, mostly silicas. About half contained a co-catalyst or modifier, such as Mo, W, Co, Ni, Na, or K. The catalysts were subjected to two reactions: hydrocracking of diphenylmethane to toluene and benzene, a model compound for the Ar-C bond cleavage of this coal structure; and hydrocracking of diphenyl ether to phenol and benzene, a model compound for the Ar-O bond cleavage of the coal structure. To enable comparison to a known commercial hydrogenation catalyst, Co/Mo/Al₂O₃ was included as a part of the series.

In general, the catalysts required the presence of hydrogen sulfide, and the commercially supplied sample of silica with its high surface area worked very well as a support. The catalysts in which the iron oxides were deposited on silica exceeded or equaled the activity of a simple admixture of iron oxide and silica. The iron oxide catalysts were better than the commercial hydrogenation-hydrocracking catalyst Co/Mo/Al₂O₃ for the hydrocracking of diphenylmethane, but the

latter exhibited both hydrocracking and hydrogenation ability. Moreover, the Co/Mo/Al₂O₃ was more active in the conversion of diphenyl ether. (University of North Dakota)

It is well known that the presence of coal may accelerate the rates of certain reactions under liquefaction conditions. It has now been found that the thermal decomposition of 1,3-diphenylpropane is also promoted by the presence of coal. The reaction proceeds by a free radical chain mechanism. Coal may act as an initiator for the decomposition reaction. The extent of decomposition of 1,3-diphenylpropane was used as a measure of the reactivity of coals and coal macerals. For macerals, the order of reactivity was exinites, vitrinites, inertinites. These correlations help to explain the differences among coals in liquefaction activity. (University of Chicago)

Mechanism and Kinetics *Sayeed Akhtar, Coordinator*

The objective is to investigate the mechanisms and kinetics of liquefaction, gasification, and combustion of coal. The scope of inquiry includes both catalyzed and uncatalyzed reactions. The results of the research are expected to lead to improvements in coal conversion and utilization processes.

A theoretical model was developed for describing the performance of bubble-column reactors used for Fischer-Tropsch synthesis. The model accounts for axial dispersion in both the gas phase and the liquid phase, and for nonuniform distribution of catalyst. The influences of H₂ and CO concentrations in the liquid phase on the stoichiometry and kinetics of the synthesis and water-gas-shift reactions were treated rigorously. Calculations were carried out to illustrate the influence of transport parameters on syngas conversion and axial distribution of reactants and products. Comparisons were also made with experimental results to demonstrate the capability of the model to predict the dependence of the syngas conversion and H₂-CO consumption ratio on feed composition and velocity. (University of California)

The change in a potassium catalyst activity during char-CO₂ and char-H₂O reactions at 700°C and 800°C was investigated. The instantaneous rate depends on both catalyst concentration (K/C) and the internal porous structure of the solid. At low values of K/C atomic ratio, the rate increases sharply with the addition of catalyst. As the catalyst concentration was increased, the rate first leveled off and then decreased. The leveling

off is attributed to the saturation of the surface with catalytic sites. The subsequent decrease in rate seems to be due to the plugging of micropores by catalyst deposits. The reaction rate changes significantly during gasification and drops sharply before gasification is complete. The drop in rate before total conversion can be explained by the catalyst accumulation, pore plugging, and a change in the solid surface area. The surface areas of the samples at various levels of conversion were measured using CO₂ adsorption at 25°C. The models that were adequate for representing the char porous structure under noncatalytic conditions were inadequate for representing catalytic gasification at low conversions. Other important factors contributing to the variation in rate during conversion are the catalyst loss and the change in the catalyst/oarbon ratio. A model has been developed that combines the effects of these contributing factors and gives a satisfactory representation of the experimental data. (University of Arizona)

A laminar-flow reactor for devolatilization-pyrolysis of coal was designed and constructed. With this reactor, the pyrolytic activity of any carbonaceous solid can be measured. The apparatus can be operated with non-corrosive carrier gases at temperatures up to about 800°C, coal feed rates of 0.5 g/min to 2.0 g/min, and pressures up to 500 kPa (5 atm). Relatively minor equipment modifications can enlarge the range of these operating parameters. (Southern Illinois University)

Studies at 375°C and 6.9 MPa showed that water, either added as such or generated in situ from an oxygenated compound, increases the rate of hydrodenitrogenation on a NiMo/Al₂O₃ catalyst. The effect occurs both in the presence and in the absence of H₂S. The promoting effect of water on the catalyst activity was reversible, although the degree of reversibility when water was removed varied with conditions. Resulfiding reduced the catalyst's activity to the level it had before the addition of water. The promoting effect of water was not proportional to its concentration; the first few kPa of water showed the most noticeable effects. (Massachusetts Institute of Technology)

Combustion experiments were conducted in a laminar-flow tubular furnace with wall temperature maintained at 1600K. The gas composition was varied in the range 13% to 40% oxygen in nitrogen, and the particle residence time was varied from 1.1 seconds to 8.8 seconds by changing the flow rate of combustion gas. The SO₂ emitted during combustion was determined by passing the combustion gases through a series of gas-

washing bottles containing a solution of 1% H_2O_2 . The retention of sulfur in the ash varied in the range 5% to 60%. The retention increased with increasing residence time and went through a maximum as oxygen concentration increased. Higher oxygen pressures produce higher particle temperatures that result in lower sulfur retention under equilibrium conditions. The opposite trend observed may be due to the higher temperatures causing ash sintering, with some of the sulfur trapped before it can be released as SO_2 . A fluidized-bed combustor was set up to study combustion at lower temperatures (1000K to 1200K) where thermodynamics favor the retention of sulfur as CaSO_4 . In experiments with calcium-exchanged lignite (Ca/S ratio of 1.7), 83.5% to 93.5% of the sulfur was retained in the ash. Further experiments are planned with calcium-exchanged bituminous coal. (CALTECH)

Three types of pulverized coal were burned in a laboratory furnace under various combustion configurations. Pulverized samples of Utah bituminous, Beulah (North Dakota) lignite, and Texas lignite coals were burned at a rate of 2.5 kg/hr in a laboratory furnace. Aerosol size distributions were measured at various positions within the convection section, and temperature and gas compositions were measured throughout. The submicron particle size distributions within the convection section for the three coals were similar, although the location of the initial particle mode at the convection section inlet varied with coal type. While staged combustion of Utah bituminous coal had a variable effect on the volume of submicron aerosol produced, staged combustion of the lignites caused a definite increase in the submicron aerosol volume. Vapor enhancement due to a localized reducing atmosphere, which would affect coals of higher ash volatility, is thought to explain this behavior. (University of Arizona)

A new method for generating alkali vapors is being exploited to simulate and investigate the reactions responsible for corrosion by coal combustion condensates. Potassium and sodium vapors were generated by reacting K_2SO_4 and Na_2SO_4 with graphite at 700°C to 1100°C in a Knudsen cell made of graphite. At these temperatures, only alkali vapors permeate through the cell walls, leaving behind the other reaction products, e.g., CO , CO_2 , K_2S , and S . The emerging vapors, at partial pressures of the order of 10^{-6} torr, were cooled to room temperature and impinged on films of CuS on Cu , $\text{Fe}_2(\text{SO}_4)_3$ on glass, and S on glass for 1 to 6 days. In every experiment, some reaction was observed. The CuS/Cu substrate un-

derwent severe corrosion, becoming very flaky. X-ray powder diffraction of the products on the substrate showed that potassium copper sulphate, potassium hydrogen sulfate, and a third unidentified component had been formed. Sodium sulfide was the principal product on the S/glass substrate. Analysis of the complex mixture formed on the $\text{Fe}_2(\text{SO}_4)_3/\text{glass}$ substrate is not yet available. (Arkansas State University)

Tetralin and a mixture of 5% phenanthrene in tetralin were hydrotreated in a two-stage trickle-bed reactor over a commercial Ni-Mo/alumina catalyst at 350°C (662°F) and 10.34 MPa (1500 psia). These runs were compared with the runs where 100 ppm of titanium as titanocene dichloride were added to the feedstocks. Both the catalyst samples and the oil samples were analyzed to measure the catalyst activity and coking. An additional run was made to check the reproducibility of experiments. Meanwhile, preliminary studies were conducted on the homogeneous reaction of tetralin with titanocene dichloride. These studies indicate a slow homogeneous reaction occurring between tetralin and titanocene dichloride at room temperatures. Hydrotreatment experiments show that the addition of titanocene dichloride to the feedstocks increases the H/C ratio of the products. Similar effects are also observed when the distillation curves of the products are compared. Addition of titanocene dichloride lowers the bubble point curves for both feedstocks. However, the effects on the coke formation depend on the hydrocarbon feedstock used. While the addition of titanocene dichloride decreases the coke formation for tetralin/phenanthrene feedstock, it gives increased coking when only tetralin is hydrotreated. Gas chromatographic analyses show that tetralin is hydrogenated to cis- and trans-decalin, with small amounts of naphthalene formed as by-products of the process. (Oklahoma State University)

Physical, Chemical, and Thermodynamic Properties of Fossil Fuel Liquids

W.E. McKinstry, Coordinator

The objective of this program is to support basic scientific research for measurement and prediction of physical, chemical, and thermodynamic (PCT) properties of synthetic liquids derived from fossil fuels. Currently sponsored work includes research at universities on PCT properties of synthetic fuels and their components, research at PETC on structural characterization of synfuels, and research at NIPER (Bartlesville) on measurement of ther-

modynamic properties of model compounds in synfuels.

The PETC in-house characterization study has completed modification and testing of the Hyper-Cal distillation apparatus in preparation for distillation of selected samples collected at the Wilsonville Pilot Plant. Duplicate test runs of a direct liquefaction product gave comparable weight percent 50°F fractions, and "simulated distillation" examination of fractions from the duplicate test runs gave comparable boiling ranges. Currently, a Wilsonville sample from Run 245 is being distilled into 50°F fractions. Experiments to study intermolecular interactions were performed to determine the utility of photometric titration of the phenolic hydroxyl modes in a coal distillate and indicated feasibility of the method.

Experimental measurements of PCT properties of model compounds representative of fossil-fuel-derived substances are continuing at NIPER. Enthalpy of vaporization measurements are underway on 2-methylpiperidine on the vapor-flow calorimeter. Very precise measurements were completed for the enthalpy of formation of chroman, isochroman, and coumaran. The vapor-phase spectrum of benzofuran is being determined for calculation of its ideal gas properties.

In the design and construction of new equipment at NIPER, appreciable progress was made in (1) the construction of a new heat-capacity calorimeter for reactive compounds, (2) the modification of the inclined-piston vapor-pressure apparatus for computer control, and (3) the design of a torsion-effusion vapor-pressure apparatus for very high molecular weight substances.

University projects include work on PCT properties measurements, correlation, and supercritical fluid characterization.

The basic instrument for viscosity measurement, the oscillating-disc viscometer, has been reassembled, modified, and proven. By way of transition, measurements were made on mixtures of two polar substances: H₂O and D₂O. The precision achieved was 0.1%.

The viscometer is working and reliable with proven procedures to secure a precision of the order of 0.1% to 0.2% and an accuracy of 0.5%. (Brown University)

The extent of desulfurization of coal using supercritical steam as a function of pressure, steam quantity, and soaking time was systematically studied in a flow microreactor. Pyritic,

organic, and sulfatic sulfur forms are removed by a first-order-rate process. About one half of the total sulfur was removed.

A flow microreactor was designed and constructed to investigate the extraction of coal with supercritical p-xylene containing such entrainers as quinoline, tetrahydroquinoline, naphthalene, and tetralin. Preliminary results with pure p-xylene at subcritical temperature (630°F) and supercritical pressure (540 psi) with solvent/coal = 11.5 ~ 39.0 mL/g showed extractions ranging from 13% to 20%.

A quantitative theory for dilute solutions near the critical point has been adapted to predict solubility as a function of temperature and pressure. A gas chromatograph is being constructed to test the separating power of supercritical fluids. (Purdue Research Foundation)

Normalization group formulations were investigated with the three-parameter corresponding states correlation of Pitzer et al. to cover molecules through three-ring coal liquid compounds from their critical points to their freezing points. Even moderately polar compounds, such as carbazole and acridine, could be correlated along with normal fluids. Work is proceeding on prediction of saturated fluid densities and liquid phase fugacity functions. Vapor pressures used in these correlations were determined experimentally by charging zone purified compounds to an equilibrium cell. (Rice University)

Isothermal flow calorimeters were assembled, tested, and calibrated to collect calorimetric data at 25°C, 100°C, and 200°C. An isoperibol titration calorimeter was assembled, tested, and calibrated to collect titration calorimetric data at 25°C and 100°C.

Calorimetric data were obtained on the molecular interactions in the following binary systems:

- Quinoline - Aniline
- Quinoline - m-Cresol
- m-Cresol - Aniline
- m-Cresol - Furan

The calorimetric data were collected at 25°C by isoperibol titration calorimetry and are currently being collected at 100°C and 200°C by isothermal flow calorimetry for these systems.

The calorimetric data are being analyzed to identify the complexes formed by the various components of the binary systems studied and to

determine the ΔG° , ΔH° , and ΔS° values for the formation of these complexes at 25°C, 100°C, and 200°C. (Brigham Young University)

Measurements were made using a bubble point pressure apparatus for the determination of liquid and vapor phase compositions in equilibrium mixtures. Experimental data at 323.2K (122°F) and 244.3K (160°F) were obtained for the solubility of carbon dioxide in n-dodecane at pressures to 5.9 MPa (850 psia). These data complete our studies of CO₂ in heavy paraffinic solvents with from 12 to 44 carbons in the paraffin chain. The data show average uncertainties of 0.002 in the measured CO₂ mole fractions (at mole fractions up to 0.500).

The data for CO₂ solubilities in heavy n-paraffins are well represented by the Soave modification of the Redlich-Kwong equation of state if binary interaction parameters are applied to both constants in the equation.

Major effort has centered on a redesign of the experimental facility for gas solubility measurements. The rocking cell in the previous apparatus has been replaced by a magnetically stirred cell. This and other minor revisions should permit data of high accuracy to be obtained at a much faster rate than is presently possible. The new apparatus has been constructed and is undergoing testing. (Oklahoma State University)

A workshop in support of the PCT Properties Program was held at the AR&TD Contractors' Review Meeting in Pittsburgh. Participants consisted of ten DOE personnel and eleven principal investigators of projects funded by PCT and related University Coal Research programs. Information exchange and discussions resulted in agreement to select two well-documented samples from the Wilsonville catalytic hydrotreater product streams (450°F to 950°F distillate and residue) for characterization studies and to select tetralin, quinoline, m-cresol, and their binary and ternary mixtures for extensive PCT measurements by the PI's. Coordination of this research will support the PI's doing correlation studies.

General Topics *Sayeed Akhtar, Coordinator*

The attritions of a metallurgical coke and several coals were investigated in a fluidized combustor under comparable conditions. Burnout times for the coke were longer than for the coals, and the loss of combustion efficiency was larger. When the burnout times of the coke were varied by changing the concentration of oxygen in the

fluidizing gas, the loss of combustion efficiency was, again, larger at longer burnout times. The loss of combustion efficiency in these experiments is believed to be due to elutriation of carbon fines. Thus, the longer the burnout time, the larger the loss of combustion efficiency due to increased detachment of elutriable carbon. (University of Naples)

The motion of solids in a gas fluidized bed was investigated with mixtures of particles of 0.5-mm and 0.8-mm average diameters. High superficial gas velocities induced good mixing. When only the large-sized particles were used, the representative probability density distribution was the same throughout the bed. For polydispersed systems, however, the representative probability density distribution was larger near the free surface and the distributor than in the bulk of the bed. (University of Illinois at Urbana)

The use of a counterflow premixed flame in an experimental study of coal pyrolysis in hot, reducing environments and at high heating rates was investigated. The opposed jet configuration has been used previously to study chemical kinetics in gaseous diffusion flames, but not until recently has it been used in heterogeneous systems. Results show that this configuration is one-dimensional in temperature and in species concentration over a fairly wide region. This characteristic simplifies both experimental and theoretical analyses. The configuration is well suited for the study of short-time-scale (on the order of milliseconds) phenomena important in coal pyrolysis, with special applications for investigation of effects at high temperatures and high heating rates. (University of Arizona)

The diffusion of a gas in a porous solid is analogous to two other classical problems: the conduction of heat in a two-phase medium, one phase being insulating; and the conduction of electricity in a two-phase medium, one phase of which does not conduct. This analogy appears to have been left unrecognized and unexploited by investigators concerned with predicting diffusion rates in porous solids. It enables the prediction to be made using the Maxwell or Bruggeman equations. Conversely, the Monte Carlo simulations of gaseous diffusion in porous solids should yield predictions of the effective conductivity of electrolytes containing gas bubbles. Some results from the new algorithm for predicting gaseous diffusion rates have been compared to the predictions of the Bruggeman and Maxwell equations. The predictions of the Monte Carlo simulations agree with these classical equations. It has

become apparent that the Monte Carlo simulations will provide "spin-offs" in other important areas of transport phenomena, besides those of diffusion in porous solids. (University of California)

The following apparatus and equipment were assembled for conducting experiments to prepare superclean coals: (1) an automatic sample splitter, (2) a computer-based induction time apparatus, (3) an attrition mill for batch and continuous grinding, (4) a collection efficiency/bubble loading apparatus, (5) a flotation kinetics apparatus, (6) a device for measuring water entrainment with air bubbles, (7) a bubble charge measuring apparatus, and (8) a continuous flotation column. Work with the equipment is under way. (VPI and State University)

Thermodynamic and Transport Properties

W.E. McKinstry, Coordinator

The objectives of the research conducted within this category are directed at developing an improved fundamental understanding of the thermodynamics of coal liquefaction. Emphasis is placed on the hydrolysis under supercritical conditions, the solute-solvent interaction under supercritical conditions, the high pressure/temperature phase and volumetric behavior of coal liquid constituents, and the role of the presence of coal-derived solids on the equilibrium compositions of liquid and vapor phases of coal liquids. Another objective is to develop thermophysical properties' correlations and characterization parameter estimation for coal fluids.

The primary products from the pyrolysis of dibenzyl ether, neat or in tetralin, are toluene and benzaldehyde, while the primary product from pyrolysis in supercritical water is benzyl alcohol. It is therefore concluded that hydrolysis reactions are important during pyrolysis in supercritical water. Similar evidence for hydrolysis during the pyrolysis of guaiacol and benzylphenylamine in supercritical water was noted. These observations indicate that the products from the extraction of coal by supercritical water will be different from those by extraction with supercritical organic solvents. (University of Delaware)

The collision-induced Rayleigh spectra of sulfur hexafluoride were studied at both below and above the critical temperature. Sulfur hexafluoride is a good compound for this study because its P-V-T data, hard sphere diameters, and diffusion coefficients are available from

literature. The Rayleigh spectra at 23°C, 80°C, and 120°C, at densities in the range 1.0 to 1.9 g/cc, were characterized by a single exponential decay constant, and the second moment and the ratio of the fourth moment to the second moment calculated. (University of Illinois)

A perturbation chromatography apparatus was used to study the vapor-liquid equilibrium behavior of six light gases in two hydrogen-coal liquid model compound systems. Infinite dilution K-values were determined for methane, ethane, propane, n-butane, carbon dioxide, and hydrogen sulfide in the hydrogen-dibenzofuran system at 373.2K and 398.2K and up to 6 MPa; and the hydrogen-9-methylantracene system at 373.2K, 398.2K, 423.2K, 448.2K, and 473.2K and up to 21 MPa. Henry's constants were determined for the light gases in 9-methylantracene. Second cross virial coefficients and vapor-phase infinite-dilution fugacity coefficients were calculated for the hydrocarbon gases in hydrogen. The results were combined with the experimental K-value measurements to obtain Henry's constants in hydrogen-9-methylantracene mixtures of fixed liquid composition. The constants showed a significant dependence on hydrogen solubility. (Rice University)

Experiments were conducted with the pure component systems of benzene, tetralin, toluene, and distilled water in order to verify that the apparatus is producing accurate experimental results. The vapor pressure of these systems was measured as a function of temperature over a range of 0°C to 350°C. The vapor pressures obtained were compared with those from literature using Antoine's Equation and Perry's Chemical Engineering Handbook. The experimental and literature values compared well, with a maximum absolute error of less than 1 psia. Presently, binary component systems are being analyzed in the absence of coal solids. Addition of coal solids to the solvent systems will enable a detailed examination of the effects of coal solids on coal liquid mixtures. (University of Pittsburgh)

A modified Local Compositional Model (LCM) was developed for the prediction of viscosity of multicomponent mixtures for polar, nonpolar, and associating coal fluids. With the introduction of this modified definition of LCM, Scott's two-fluid theory, originally developed for the prediction of equilibrium thermodynamic properties such as Gibbs energy, can successfully be applied for predicting nonequilibrium transport properties such as viscosity. The model is capable of predic-

ting viscosity for vapor phase as well as liquid phase mixtures. Predictions based on the model for several binary mixtures, including those in

which strong associating forces prevail, show excellent agreement with experimental data. (University of Oklahoma)

IN-HOUSE RESEARCH AND DEVELOPMENT

AR&TD: COMBUSTION

J.M. Ekmann, Coordinator

This activity consists of four projects that deal with a broad gamut of combustion-related problems. These problems range from fuel handling through ignition and combustion to the fate of the mineral matter in the coal. The dense-phase powder characteristics project seeks to develop fundamental data on coal powder flow characteristics on a laboratory scale, particularly on those properties important in dense-phase transport. The project examining flow characteristics of coal-based fuels seeks to develop engineering data on flow properties of coal-water and coal-gas systems in a flow-loop facility. Combustion characteristics of cleaned and micronized coals are being investigated to determine the effects that firing beneficiated and/or micronized coal in a pulverized or slurried form have on particulate processes occurring during combustion. Finally, a project is under way to evaluate various measurement techniques capable of monitoring the physical and chemical structure of deposits as a function of time.

Shear stress measurements on size-classified samples of pulverized coal were made. It was noted that the peak and ultimate shear strengths of Pittsburgh seam coal and Illinois coal samples were reduced for the fine-size fraction (below 43 microns) compared to the as-received samples. In the flow-loop facility, flow tests with a vinyl coating powder, instead of coal, were conducted in an effort to run flow visualization studies in the elbows.

Modifications were made to the tunnel furnace to incorporate cooling surface. By varying the insertion depth of the cooling surface, different cooling loads can be simulated. Feasibility testing of an eddy current technique for deposit property measurements was initiated. Eddy current measurements as a function of deposit thickness and composition were conducted.

Dense-Phase Powder Characteristics

M.P. Mathur, Cost Account Manager

J.I. Joubert, Chief,

Combustion Technology Branch

The overall objective of the study is to develop fundamental data on coal powder flow characteristics applicable to the development of a system

for direct combustion of dense-phase streams of pulverized coal. A laboratory-scale study will be carried out to study flow properties as a function of the particle-size distribution, coal type, coal moisture content, particle size, and coal blends. Stress-strain rates studies will be conducted.

It is becoming more evident that current techniques of flow classification provide only a partial answer to the problems of systems design. For example, the use of Zenz and Othmer two-phase flow diagrams in conjunction with Geldart's classification can only provide an indication of mode of flow. From a recent study,¹ it is clear that these two classifications are insensitive to aspects such as particle density and particle shape. Thus, a finer understanding of such powder characteristics as aerated-bulk density; packed-bulk density; compressibility; cohesion; angles of repose, difference, spatula, and fall; dispersibility; floodability; and flowability is required. Moreover, the frictional characteristics between the particles and between particles and wall should be determined. To accomplish this, the coefficient of friction or angle of internal friction of various powders should be measured using a shear cell tester.

During this quarter, two samples of Pittsburgh seam coal (float 1.3 and float 1.5) and one sample of Illinois No. 6 coal (float 1.6) were pulverized in our coal-processing unit. The samples were classified into various size ranges using a jet sieve. Shear stress as a function of displacement at various normal loads was measured for the as-received samples as well as the fines samples, with particle size less than 43 microns. From these data, the peak shear strength (ϕ_M) and ultimate shear strength (ϕ_U) of the samples were determined. These values are listed in Table 11. It is noted that the peak strength as well as the ultimate strength of the as-received samples is reduced by about 35% for both Pittsburgh seam coal samples and by about 17.5% for Illinois coal sample when samples are finely ground (particle size <43 microns). It seems the fines in the sample provide a sort of lubricating effect. Shear tests with various blends of powders will be of interest

1. C.L. Snow, M.S. Thesis, March 1984, University of Witwatersrand, S.A.

Table 11.
Angle of Internal Friction

Samples		ϕ_M Peak	ϕ_U Ultimate
A.	Pittsburgh Seam Float 1.3		
	1. As-Received	$42.8^\circ \pm 2.1^\circ$	$41.5^\circ \pm 1.5^\circ$
	2. Fines (particle size <43 microns)	$27.9^\circ \pm 3.7^\circ$	$25.6^\circ \pm 4.5^\circ$
B.	Pittsburgh Seam Float 1.5		
	1. As-Received	$43.9^\circ \pm 1.8^\circ$	$43.0^\circ \pm 1.7^\circ$
	2. Fines (particle size <43 microns)	$29.1^\circ \pm 1.2^\circ$	$28.1^\circ \pm 0.9^\circ$
C.	Illinois No. 6 Float 1.6		
	1. As-Received	$39.3^\circ \pm 6.1^\circ$	$38^\circ \pm 1.9^\circ$
	2. Fines (particle size <43 microns)	$32.4^\circ \pm 1.7^\circ$	$31.6^\circ \pm 1.3^\circ$

to fully understand the mechanism of flow and the part played by the fines. Other mechanical properties of these powders were also measured. These results will be discussed in the next quarterly.

Flow Characteristics of Coal-Based Fuels

D.J. Wildman, Cost Account Manager

*J.I. Joubert, Chief,
Combustion Technology Branch*

In April, shakedown tests were performed on the High Pressure Test Loop using steam as the transport gas. Formal testing will begin when all the high-temperature instrumentation is received.

In May and June, tests were begun to study the development of secondary flow patterns around bends and elbows for solid-liquid transport. A vinyl coating powder with specific gravity of 1.3 and size distribution of 85% finer than 75 microns was mixed with water and used in these tests. Visualization of flow patterns around bends and elbows was possible. Secondary flow patterns were observed in a standard 90-degree elbow. No secondary flow patterns were visible in tests conducted with long-radius bends.

A paper entitled "Flow Characteristics and Handling Properties of Commercial Coal-Water

Mixtures" was presented at the Sixth International Symposium on Coal Slurry Combustion and Technology.

Combustion Characteristics of Cleaned and Micronized Coals

R.J. Walker, Cost Account Manager

*J.I. Joubert, Chief,
Combustion Technology Branch*

The objectives of this project are to investigate the effects of firing beneficiated and/or micronized coal in a pulverized or slurried form has on particulate processes occurring during combustion, and to assist the Advanced Research Contracts Branch in developing a technology base for the utilization of cleaned and micronized coals, with emphasis on information required for design and performance prediction of oil/gas designed combustion equipment in a coal-firing mode of operation.

Previous problems in maintaining combustion of CWM without natural gas were traced to low firing rates (1.5-lb CWM/minute). Consequently, four cooling coils were installed in the furnace to permit higher firing rates. Inadequate secondary-air preheat was also suspected, so the controls were

modified to permit 550°F preheat. A new carbide-lined burner nozzle was purchased and installed.

Cold spray tests of the old and new burner nozzles were conducted, revealing inadequate atomization by the old burner nozzle at a CWM flow of 1.5 lb/minute and a realistic atomization air/slurry ratio of 0.53. The new nozzle was satisfactory.

Combustion tests of the old and new burner nozzles, which were both water-cooled, revealed persistent plugging problems, apparently due to tip heating causing the evaporation of some of the water from the CWM before it could be atomized. Measures to correct this are being evaluated, especially the use of a high-thermal-conductivity alloy for the nozzle body and tip, and use of soft-metal gaskets to minimize thermal-contact resistance. The combustion tests also revealed that the secondary-air blower had marginal head for the high-swirl air register, although it was usable at a CWM flow of 1.5 lb/minute.

The computer program to evaluate air register design was modified to handle curved vanes rather than flat vanes. This had a drastic effect on calculated-swirl number. The results will be checked by a different (and more complicated) curved-vane model.

Technique Development for Slagging and Fouling Characteristics

M.P. Mathur, Cost Account Manager

J.I. Joubert, Chief,

Combustion Technology Branch

The objective of the study is to evaluate various measurement techniques capable of monitoring the physical and chemical structure of deposits as they are formed and as they change with time within a coal combustor.

In the last quarterly, X-ray diffraction data and Mössbauer spectroscopic data on four real deposit samples were discussed. Both of these analyses indicate the presence of magnetite in the samples. The magnetic properties of the ox-

ides in the deposits can be exploited to design probes for slagging/fouling phenomena. A feasibility study of using magnetic oxides for measurement application was carried out.

Applications for Eddy current testing have grown over the years as the understanding of and sensing of inductive impedance has become more sophisticated. At present, quality control for tubing — especially exotic thick-wall types — is routinely done with Eddy current probes checking for flaws, wall thickness, and concentricity. An Eddy current device that exploits the magnetic properties of coal ash deposits is under investigation.

PETC has conducted feasibility testing of an Eddy current technique for measuring deposit thickness in situ. The method consists of measuring impedance changes in a flat coil caused by Eddy currents induced in a magnetic or electrically conductive material. These measurements were conducted in the frequency range of 100 Hz to 100 kHz and as a function of deposit thickness.

In Figure 1, a typical Eddy current signal as a function of thickness for an Fe_3O_4 sample is given. It is noted from the figure that most of the attenuation of signal takes place within a layer of thickness of 0.1 inch, and the resolution of the signal is best at 100 kHz.

In Figure 2, a typical graph of the attenuation of the Eddy current as a function of the slag deposit thickness for various frequencies (100 Hz, 1 kHz, 10 kHz, and 100 kHz) is given. The layer thickness in which most of the attenuation takes place is between 0.4 and 0.5 inches. Again, the measurement sensitivity at higher frequency (10 kHz and 100 kHz) is better than at lower frequency (100 Hz and 1 kHz). Preliminary data obtained at room temperature indicate good potential for using the technique for monitoring deposits in boilers, thereby permitting optimal usage of ash removal equipment. A paper giving details of various tests was presented at the First AR&TD Surface Coal Gasification meeting held at Lakeview Inn, Morgantown, W.Va., on June 13 and 14, 1984.

FIGURE 1. GRAPH OF Fe_3O_4 SAMPLE M1
1/16" Stainless Steel Substrate

FIGURE 2. GRAPH OF SLAG SAMPLE
1/16" Stainless Steel Substrate

AR&TD: STRUCTURAL ASPECTS OF LIQUEFACTION

R.G. Lett, Coordinator

This program encompasses projects concerned with the determination of fundamental properties of direct liquefaction products, particularly non-distillate fractions, and hydrogenation catalysts. These investigations will provide information needed to achieve a deeper understanding of coal dissolution and liquefaction chemistry, develop correlations between catalyst activity and structure, and improve predictions of the thermophysical properties of high-boiling and non-distillate coal-derived materials.

Structural relationships between feed coals and toluene-insoluble fractions of first-stage products from two-stage liquefaction experimentation were investigated. Carbon and hydrogen aromaticities of the insolubles from both short- and long-residence-time products of Illinois No. 6 coal were significantly higher than those of the feed coal. The toluene insolubles thus represent fragments from hydrogen-depleted domains of the original coal or fragments of the original coal that have undergone additional dehydrogenation or condensation reactions after thermal cleavage of weak cross-links. An increase in protonated aromatic hydrogen and hydrogen aromaticity of the toluene insolubles with residence time followed the trend expected on the basis of reaction severity.

Magnetic resonance studies of the interaction of coal with polar compounds were initiated. Investigation of the interaction of pyridine with Illinois No. 6 coal by advanced ^{13}C nuclear magnetic resonance techniques for solids reveals substantial changes in the coal matrix after a cycle of pyridine absorption and removal.

In research related to the thermophysical properties of synfuels, wide ranges of chemical and physical properties of pseudocomponents from an H-Coal liquefaction product were determined and correlated with boiling point. Predictive correlations, developed for petroleum pseudocomponents, were used with reasonable success to predict properties of the H-Coal pseudocomponents. Fractionation of a high-boiling two-stage liquefaction product from the Wilsonville Advanced Liquefaction Facility into 50°F boiling range cuts is in progress.

The improved separation achieved by recent refinements in fractional distillation unit operating parameters has been demonstrated by the molecular weight profiles of fractions col-

lected from Wilsonville vacuum bottoms under reflux conditions. Molecular weight data from vapor phase osmometry and field ionization mass spectrometry are being used to calibrate a more rapid gel permeation chromatography procedure for following the fractionation. Activity coefficient data have been obtained for a binary mixture of o-ethylphenol and coal-derived residuum using headspace chromatography.

Studies were begun to determine the effect of various promoters on the structure of alumina-supported catalysts and the effect of changing the catalyst support. Experiments are in progress to clarify the role of water and hydrogen bonding in producing $\text{Mo}=\text{O}$ frequency shifts in Raman spectra of alumina support catalysts.

Structural Changes During Coal Dissolution

R.G. Lett, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective is to gain a further understanding of liquefaction chemistry by determining changes in the fundamental structural features of coal and coal dissolution products under conditions of varying reaction severity. Advanced structural specific techniques applicable to high-molecular-weight, highly functional coal-derived materials are used to investigate the heteroatom functionality and carbon skeletal structure of products from two-stage liquefaction and selected low severity and/or short residence time experiments.

This quarter, carbon-13 cross-polarization/magic angle spinning (^{13}C -CP/MAS) nuclear magnetic resonance (NMR) techniques were extensively applied to investigate structural relationships between feed coals and first-stage products. Initially, the validity of the parameters derived by the conventional ^{13}C -CP/MAS experiment and the dipolar-dephasing extension thereof was checked using two Illinois No. 6 coal-derived SRC's from Wilsonville non-integrated two-stage liquefaction (NITSL) Runs 236 (low severity) and 241 (moderate severity). Carbon aromaticities and ratios of protonated to non-protonated aromatic carbons determined from ^{13}C -CP/MAS spectra of the solids were in very satisfactory agreement with determinations from high resolution ^1H NMR spectra in dilute pyridine solutions.

The Illinois No. 6 (Burning Star) coal associated with two-stage liquefaction experimentation at the LUMMUS and Wilsonville liquefaction facilities, and a Kentucky 9/14 coal blend used in PETC experimentation were also analyzed by ^{13}C -CP/MAS techniques. Both coals have similar carbon aromaticities, 0.71 and 0.70, respectively, but dipolar-dephasing data indicate a significantly higher fraction of protonated aromatic carbons in the Kentucky 9/14 coal. These observations imply a lower degree of aromatic ring substitution in the Kentucky 9/14 coal and would be consistent with the presence of fewer aliphatic groups directly attached to the aromatic rings or a smaller average aromatic ring cluster size than in the Illinois No. 6 coal.

The relationship of toluene insolubles from Wilsonville NITSL (long residence time) Run 241 and the first-stage product of ITSL (short residence time) Run 242 to the Illinois No. 6 feed coal was also investigated. The carbon and hydrogen aromaticities of both insoluble fractions are significantly higher than those of the feed coal. This indicates that the toluene insolubles represent either fragments from hydrogen-depleted domains of the original coal or fragments of the original coal that have undergone additional dehydrogenation or condensation reactions subsequent to cleavage of weak cross-links. A slightly larger fraction of the aromatic carbons appears to be protonated in the insolubles from the longer residence time product than in the insolubles from the shorter residence time product, consistent with more extensive dealkylation at higher reaction severity. Structural parameters derived from the toluene insolubles are in agreement with those deduced from ^1H NMR spectra of toluene-insoluble/pyridine-soluble fractions of the samples. However, the ^{13}C -CP/MAS technique has the distinct advantage of not requiring solubility, and it is free of problems due to the presence of residual mobile solvents such as toluene because they are not readily observable under CP/MAS conditions.

Derivatization and FT/IR procedures are being implemented to follow changes in phenolic OH upon coal dissolution. Relative OH concentrations have been established in Illinois No. 6 coal, Kentucky 9/14 coal, and several toluene-insoluble and preasphaltene fractions derived from liquefaction of these coals under both high severity and very mild severity conditions. Absolute quantitation is almost complete and is based upon results from polymers of known phenolic OH content, methylene chloride soluble SRC fractions previously analyzed by near-infrared procedures,

and cross-checks with the Pennsylvania State University Polymer Science Section on several samples.

Next quarter, research will continue to focus on toluene-insoluble fractions of two-stage liquefaction products and primary preasphaltenes produced from the dissociation of coal under very mild severity conditions. Changes in the carbon skeletal structure will be investigated further by ^{13}C -CP/MAS techniques. Concurrently, the differences in phenolic OH between the original coals and the heavy coal dissociation products will be determined by FT/IR methods.

Structural Mobility of Treated Coals and Coal Slurries

R.F. Sprecher, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective is to investigate coal-solvent interactions at the molecular level during the initial stages of liquefaction. Such interactions are poorly understood except in a general phenomenological sense as reflected by coal-swelling behavior and slurry-viscosity changes. These interactions can potentially be probed by using magnetic resonance techniques to study changes in the relative freedom of motion of coals after careful pretreatment over a range of temperatures or by in situ observations in coal slurries that can be related to changes in molecular motion. The results may be related to the ability to overcome mass transfer limitations in donor-solvent liquefaction and to whether thermolysis results in low molecular weight fragments or condensation to residue.

Studies are being conducted to investigate, in detail, the effect of a variety of polar compounds on the ^{13}C -NMR signals from bituminous coals, such as Illinois No. 6 and Pittsburgh seam. In particular, the utility of various NMR methods, with emphasis on data accuracy, and specialized data acquisition procedures are being investigated. Measurement protocols, including procedures for dipolar-dephasing measurements, have been established for the Brücker CXP100 NMR spectrometer.

A sample of Illinois No. 6 coal was allowed to imbibe pyridine vapor for an extended period of time. The resulting sample showed sharp NMR resonance lines, characteristic of pyridine, which are thought to arise from loosely bound pyridine. That pyridine was removed under a stream of nitrogen. The remaining sample showed two broad

NMR resonance lines thought to be due to bound pyridine. Dipolar-dephasing measurements revealed substantial changes in the coal after the cycle of pyridine exposure when compared to the original coal. The fraction of carbon in aromatic sites and bearing hydrogen decreased from 0.24 in the coal to 0.17 in the treated coal, while the fraction of carbon in methyl groups decreased from 0.12 in the coal to 0.07 in the treated coal. The relaxation time for dephasing of non-protonated aromatic carbons decreased from 300 μ s in the coal to 146 μ s in the treated coal, implying that the coal matrix is more rigid after pyridine treatment than it was before treatment.

During the next quarter, similar NMR measurements will be made on the subject coal during and after treatment with tetrahydroquinoline process solvents. Exploratory ESR experiments using spin-labeled molecules as probes of the microscopic viscosity in "gel phase" coal-solvent mixtures have been started and will be continued in the following quarter.

Structural Definition of Synthetic Fuels

C.M. White, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The purpose of this research, related to thermophysical properties of synfuels, is twofold. The first is to identify, develop, and apply advanced methods of structural characterization of synfuels that will provide data to be used in thermophysical property correlations. The information obtained by the application of these methods can be used to relate the thermodynamic behavior of pseudocomponents to that of measured, defined systems, e.g., pure component and binary mixtures. Use of the data will also permit the assessment of specific intermolecular forces. The second purpose is to identify statistically determined "most likely" or "most representative" chemical structures in the pseudocomponents of a particular synfuel. These results will be used in the choice of compounds to be produced in a synthetic organic chemistry project that is funded as part of the overall Physical, Chemical, and Thermodynamic Properties of Synfuels program.

A well documented H-Coal sample was selected for initial study. The sample was produced at the Catlettsburg H-Coal Pilot Plant on September 25, 1981, while processing Illinois No. 6 coal in the synfuel mode of operation. A blend of "light oil" and "heavy oil" products (1:1.5) was distilled at Chevron into narrow-range distillates.

Specifically, 50°F cuts were obtained in the boiling range of 400°F to 850°F; the start to 400°F material and the 850°F+ material were also obtained. Sufficient amounts of each distillate were obtained for analytical purposes.

In addition, two well-documented sets of samples have been acquired from the Advanced Coal Liquefaction Facility in Wilsonville, Ala. Samples were taken from all the process streams of both Run 245 (bituminous coal, ITSL mode) and Run 246 (subbituminous coal, DITSL mode).

The Hyper-Cal distillation apparatus has been modified successfully and tested using a direct liquefaction product similar to the two Wilsonville products that will ultimately be distilled into 50°F distillates (pseudocomponents). This test sample was distilled three times. The first distillation was used to debug the system and train the operators, while the second and third experiments were performed to obtain a measure of our ability to reproduce the results. The weight percents distilled from start to 500°F and over 50°F boiling ranges between 500°F and 700°F were quite comparable for the duplicates. Examination of the 50°F distillates from the duplicate distillations by "simulated distillation" showed that the temperatures at which 10%, 50%, and 90% of the material boiled were also comparable. Currently, a Wilsonville 650 x 950 sample (Run 245, produced during December of 1983) is being fractionated into 50°F distillates. In addition, vapor-liquid equilibrium measurements are also being obtained on this material.

General Inspection properties, including CHONS, VPO molecular weight, FPD molecular weight, mass spectral molecular weight, water content, pycnometric specific gravity at three temperatures, viscosity, refractive index, quantitative hydroxyl content, and simulated distillation by gas chromatography were determined for the H-Coal pseudocomponents. Each H-Coal pseudocomponent was also examined by various advanced chromatographic and spectrometric analytical measurements. The proton distributions were measured by ¹H NMR, and carbon aromaticities were calculated. Infrared spectroscopy has been used to survey the functional groups present, to quantitatively determine the OH concentrations, and to estimate the amounts of -NH in each pseudocomponent. All pseudocomponents have been separated chromatographically into saturates, aromatics, acids, and bases. The quality of these separations has been monitored by Fourier Transform Infrared Spectrophotometry. This monitoring procedure showed that there was some overlap among chromatographic fractions.

In cases where the overlap of chromatographic fractions was severe, the separations are being repeated. When clean chromatographic fractions of the pseudocomponents are obtained, these materials will be studied by gas chromatography and various spectroscopic methods. High resolution, low ionizing voltage mass spectrometry yielded the molecular formulae for individual constituents present in each pseudocomponent. Low resolution field ionization mass spectral measurements were made on the 850°F + bottoms to obtain mass information on the nonvolatile fractions. PETC is collaborating with the National Institute of Petroleum and Energy Research (NIPER) in developing high resolution field ionization mass spectrometry (HRFIMS) as a useful characterization tool for nonvolatile coal liquefaction residua.

The analytical information obtained has been correlated with each fraction's mid-boiling point (temperature at which 50 wt% of the sample distilled). Analysis of these data revealed good correlations between the boiling points of the fractions, and the various physical and chemical properties.

Many correlations exist within the data. Predictive correlations originally developed for petroleum pseudocomponents have been used to predict, with reasonable accuracy, the properties of the H-Coal pseudocomponents. Specifically, equations developed by Huang have been used to predict the refractive indices of the H-Coal pseudocomponents. The predicted and experimentally determined results are in Table 12. Similarly, four correlations found in the literature that allow the prediction of a pseudocomponent's average molecular weight based on measurement of other properties were evaluated. The equations evaluated were those developed by Huang, Gray, Brule', and Wilson. Preliminary comparisons among the predicted average molecular weights and the experimentally determined values indicate that, in general, Gray's correlations produced the best results. Table 13 compares the predicted average molecular weights using Gray's equation with those measured by VPO and FPD. There is good agreement between the predicted and experimentally determined values. Evaluation of the analytical measurements made on the H-Coal distillates is continuing, and additional correlations are being sought.

Table 12.
Experimentally determined and predicted refractive indices of H-Coal pseudocomponents using correlations developed for petroleum distillates by Huang

Boiling Range (°F)	T _b °F (°R)	n Experimental ^b	n Predicted ^a	$\frac{ Pre-Exp }{Pre} \times 100$
				% Deviation
400-450	429 (888.7)	1.5206	1.5480	1.77
450-500	465 (924.7)	1.5295	1.5407	0.73
500-550	509 (968.7)	1.5357	1.5447	0.58
550-600	561 (1020.7)	1.5623	1.5548	0.48
600-650	613 (1072.7)	1.5646	1.5764	0.75
650-700	662 (1121.7)	1.5873	1.5936	0.40
700-750	712 (1171.7)	1.6267	1.6231	0.22

^aThese predicted values were generated using correlations developed by Huang carrying all digits (significant and otherwise) through the entire calculation and rounding the final answer to five significant figures.

^bNo attempt was made to dry the low-boiling distillations before the refraction indices were measured.

Table 13.

Comparison of average molecular weight of H-Coal pseudocomponents predicted using Gray's equation with the experimentally determined VPO and FPD measurements

Boiling Range, °F	Predicted Molecular Weight	VPO MW.	% Deviation From VPO Pred-Exp	FPD MW.	% Deviation From FPD Pred-Exp
			Pred		Pred
St.-400	134.38	137	1.95%	152	13.11%
400-450	143.98	144	0.01%	147	2.10%
450-500	156.71	161	2.74%	169	7.84%
500-550	172.92	176	1.78%	189	9.30%
550-600	188.54	196	3.96%	199	5.55%
600-650	208.08	213	2.08%	209	0.16%
650-700	223.18	234	4.85%	220	1.42%
700-750	235.07	250	6.35%	233	0.88%
700-775	246.78	259	4.95%	248	0.49%

Plans for the next quarter include (1) completion of the distillation of the Wilsonville 650 x 950 samples for both a bituminous and subbituminous coal; (2) chromatographic separation of the pseudocomponents from both distillations; (3) fractionation of a Wilsonville vacuum still bottoms sample by supercritical extraction and by distillation at very low vacuum in a wiped wall still (temperature range of 950°F x 1350°F at atmospheric pressure); and (4) a literature survey and preliminary experiments on characterizing charge transfer complexes using electron spin resonance spectroscopy.

Liquefaction Bottoms Characterization

R.P. Warzinski, Cost Account Manager

J.A. Ruether, Chief,

Coal Conversion Engineering Branch

The objective of this project is to apply the most suitable of a wide variety of chromatographic techniques to the characterization of non-distillable coal-derived materials. The goals are to (1) develop liquid chromatography as a relatively rapid method, in comparison to sophisticated spectroscopic techniques, for obtaining characterization data that will be useful in describing

vacuum bottoms for engineering purposes and to establish correlations between such chromatographic results and thermophysical properties of importance in the design and operation of vapor/liquid separation units used in coal liquefaction facilities; and (2) use gas chromatography to measure some vapor/liquid equilibrium properties of binary mixtures of bottoms fractions with distillates. The properties to be measured are activity coefficients and distribution coefficients of the distillate component in the binary (distillate/bottoms fraction) mixtures. Such measurements will permit a check on the accuracy of the thermodynamic treatment of vacuum bottoms.

During this quarter, field ionization mass spectral (FIMS) data were received for one of the first runs in which a Wilsonville vacuum bottoms sample was fractionated in the Fractional Distraction Unit (FDU) under reflux conditions (Run FDU33). For details on this experiment, see the January-March 1984 quarterly report on Bottoms Fractionation (DOE/PETC/QTR-84/2). The FIMS data are summarized in Figure 3 as traces of the profiles for the fractions analyzed. Table 14 presents the molecular weight averages obtained by FIMS, vapor pressure osmometry (VPO), and gel permeation chromatography (GPC).

Figure 3 - Summary of field ionization mass spectra for FDU 33

Table 14.
Summary of Molecular Weight Determinations for Run FDU33.

Fraction	$\bar{M}_N$ FIMS	$\bar{M}_N$ VPO	$\bar{M}_N$ GPC	$\bar{M}_W$ FIMS	$\bar{M}_W$ GPC
1	398	389	322	428	442
2	413	413	336	444	465
3	440	433	356	471	513
4	467	481	390	501	571
5	538	588	506	576	862
6	554	638	535	588	992

The MN determinations by FIMS and VPO agree for the first several fractions but differ for the last two fractions. Inspection of the FIMS data shows that a considerable portion of fractions 5 and 6 are beyond the calibrated mass range of the instrument. The MW in Table 14 determined by FIMS and GPC dramatically demonstrate the inability of FIMS to handle the heavier residuum fractions. In order to have a reliable, rapid method, the GPC calibrations will be "tuned" to match the FIMS and VPO data for the lighter fractions.

The fractions from recent experiments in the FDU were analyzed by GPC. These experiments were performed using more refined operating parameters in the FDU. For details, see the companion quarterly report entitled Bottoms Fractionation. Figures 4 and 5 depict the results for experiments in the nonreflux and reflux modes, respectively. The effect of using reflux to promote fractionation is obvious from the GPC profiles. The polydispersity ($\bar{M}_w/\bar{M}_n$) of the current fractions is lower than that observed for the corresponding fractions previously obtained. This indicates that the current fractions are sharper or better defined. The biggest advantage of the GPC technique is that these results were obtained the same day that the set of fractions became available. The corresponding VPO and FIMS data will take several weeks to obtain from outside sources. Operation of the FDU would be practically impossible without this means of tracking the fractions obtained.

Additional activity coefficient data have been collected using headspace chromatography for binary systems in which one component is a coal-derived material. Results reported last quarter for a binary mixture of o-cresol and a residuum prepared under relatively mild conditions (250°C, 1 torr) at PETC showed consistent negative deviation from Raoult's law. Similar experiments this quarter using o-ethylphenol in place of the o-cresol exhibited a positive deviation. Further investigation of this observation is under way to determine the utility of such measurements in the study of the phase behavior of coal-derived residuum. The fractions recently generated from the Wilsonville residuum will be studied with these two phenols.

Plans for next quarter include continuation of the characterization of fractions now being produced in the FDU. Additional liquid chromatographic techniques will be developed to focus on the aromaticity and chemical functionality of the residuum fractions. The activity coefficient determinations will be continued as discussed above.

Vibrational Spectroscopic Studies of Coal Conversion Catalysts

L.E. Makovsky, Cost Account Manager

**H.L. Retcofsky, Chief,
Analytical Chemistry Branch**

The objective of this investigation is to determine molecular structural characteristics of coal conversion catalysts that are associated with liquefaction activity. Study of the activated form of catalysts, including reduced and sulfided states, will be emphasized. The immediate goal is to record and interpret Raman spectroscopic data on catalysts in oxide, reduced, and sulfided states. Molecular speciation as a function of hydrogen and sulfide titration will be determined to ascertain correlations between catalytic activity and molecular structure.

Raman spectroscopic results that show a frequency dependence of the molybdenum-oxygen stretching frequency upon surface hydroxyl content in alumina-supported catalysts are still under investigation. Last quarter, it was reported that methanol, which does not act as a strong ligand but can hydrogen-bond, lowers the Mo=O stretching frequency to 947 cm^{-1} from 1008 cm^{-1} in the calcined state. This suggested that hydrogen-bonding effects were responsible for the observed frequency shifts. However, this explanation has been questioned because of the possibility of an H_2O contaminant in the methanol. To resolve this question, a 1-Inch x 48-Inch stainless steel drying column with 2 3/4-inch conflate flanges has been constructed and filled with a molecular sieve capable of adsorbing H_2O but not CH_3OH . The experiments are being repeated by passing the CH_3OH through the column before adsorption onto the Mo/ Al_2O_3 catalysts.

The effect of promotor size is currently being investigated for a series of molybdenum on alumina catalysts containing various elements (Ca, Na, Ce, Fe, Mn, Mg, Pb, Co) as promoters. The effect of changing the support (Al_2O_3 , SiO_2 , and ZrO_2) in catalysts having rhodium as the active metal is also being investigated.

A Raman cell for in situ experimentation on catalysts under a gas flow or vacuum at temperatures to 500°C while rotating the sample has been constructed. Initial tests were performed and minor modifications are in progress before proceeding with further experimental work.

A manuscript entitled "A Surface Spectroscopic Study of Co-Mo/ Al_2O_3 Catalysts Using ESCA, ISS, XRD, and Raman Spectroscopy, Part I"

Figure 4- GPC of Wilsonville vacuum bottoms fractions prepared without reflux

Figure 5- GPC of Wilsonville vacuum bottoms fractions prepared with reflux. Weight average molecular weight given in parenthesis

has been accepted for publication in the Journal of Catalysis. Two additional publications, co-authored with personnel from the University of

Pittsburgh, concerning Ni-W/Al₂O₃ catalysts and quantitative determination of crystalline MoO₃ by Raman spectroscopy were prepared.

AR&TD: MECHANISTIC ASPECTS OF LIQUEFACTION

B.C. Bockrath, Coordinator

Liquefaction of an Illinois No. 6 coal with water present as a major component was studied as a function of several process parameters. Relatively high conversions of coal were obtained at very low ratios of oil to coal if water is also present. Hydrogen pressure is also an important variable. Conversions increased significantly for liquefaction at 370°C when the cold hydrogen pressure was increased from 800 to 1200 psi. The addition of a small amount of ammonium paramolybdate as catalyst further increased conversions. This response of conversion to hydrotreating conditions at a relatively low temperature encourages further efforts to improve yields.

The extent of vehicle incorporation during conventional liquefaction was studied as a function of heating conditions using a synthetic solvent composed of six different model compounds. Rapid, gradual, and very slow programs of heating to 425°C were employed. The results indicate that the heat-up mode does not influence the amount of vehicle incorporation, but that time at temperatures above 350°C may be the most important variable. Further increases in vehicle incorporation occurred when the time at 425°C was prolonged to 6 hours. Apparently the incorporation of solvent into coal fragments is irreversible.

The reactions of hydrogen atom under liquefaction conditions were explored using various substituted aromatic compounds under hydrogen pressure. Bibenzyl is a suitable initiator if present in high concentration. Some of the benzyl radicals produced by its thermal decomposition attack molecular hydrogen to generate hydrogen atoms and toluene. Hydrogen atoms attack other aromatic compounds in solution, including 1-methylnaphthalene, to produce naphthalene and methyl radical. This sequence of reactions leads to the demethylation of aromatic rings and is also probably important in determining the extent of methane gas formation in coal liquefaction.

The role of catalyst in hydrogen utilization during liquefaction is being probed by analysis of the total reaction products using a combination of solvent separations, elemental analyses, and NMR spectroscopy. The objective is to compare

the action of molybdenum and tin chloride catalysts against thermal liquefaction in terms of hydrogenation, heteroatom removal, gas make, and matrix bond cleavage.

Investigation of Hydrogen Utilization

D.H. Finseth, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective is to investigate the pathways for hydrogen consumption and redistribution under different liquefaction conditions. An approach has been formulated for quantitatively determining the consumption of hydrogen via different modes of reaction, including hydrogenation, matrix bond cleavage, and heteroatom removal. Knowledge of the relative importance of these modes would facilitate development of improved liquefaction strategies to minimize hydrogen usage.

Internal PETC review of a manuscript describing the analytical method for following hydrogen utilization and its application to the study of changes in utilization with reaction temperature was completed. A few minor revisions are being made before submission to Fuel.

Experimental effort during this quarter has focused on work-up of reactor runs designed to determine the role of catalyst in hydrogen utilization. Nine autoclave runs have been made using both tin chloride and ammonium molybdate catalysts. These data are being compared with thermal runs to determine the changes in hydrogen utilization effected by the catalysts. Although the data are not yet complete, elemental analyses indicate the expected greater hydrogen incorporation with the molybdate catalysts. Solvent separations and elemental analyses of the fractions are complete, and CP ¹³C NMR analysis of the CH₂Cl₂ insoluble fractions is in progress. High resolution ¹³C NMR analysis of the soluble fractions has been scheduled.

Next quarter, the collection of the data from the catalytic runs will be completed. Experiments are currently being developed to study the extremes

of hydrogenation and dehydrogenation of slurries. This work is an attempt to check the ^{13}C NMR analysis against independent methods.

Mechanism of Coal Liquefaction

B.C. Bockrath, Cost Account Manager

*B.D. Blaustein, Chief,
Process Sciences Branch*

The objective is to provide a basis for improvements in currently used liquefaction technology by investigating the basic chemistry of coal liquefaction reactions. Particular objectives are to determine the changes in distribution of hydrogen between coal, solvent, and residues during the early stages of liquefaction; to follow the course of hydrogen transfer reactions that involve the hydrogen atom; and to study the relationship between coal conversion and the rheological properties of coal/solvent slurries at elevated temperatures.

Exploratory experiments were conducted to investigate the role of hydrogen atom reactions under liquefaction conditions. Work in other laboratories has established that certain cleavage reactions involving attack by hydrogen atoms may be initiated by the decomposition of bibenzyl under a hydrogen atmosphere. Our preliminary results provide evidence that the dealkylation of 1-methylnaphthalene can take place by a similar mechanism. In these studies, bibenzyl was decomposed in 1-methylnaphthalene at 450°C under hydrogen pressure. The yields of naphthalene and methane increased with increasing bibenzyl concentration and with increasing hydrogen pressure. The involvement of both of these components in the demethylation reaction is best explained by considering bibenzyl as an initiator by virtue of its thermal decomposition into benzyl radicals. These radicals attack hydrogen molecules to form toluene and hydrogen atoms. Hydrogen atoms then attach to 1-methylnaphthalene at the 1-position, and methyl radical is expelled from this intermediate to leave naphthalene. Methyl radical may again attack hydrogen and establish a chain reaction or attack another source of hydrogen in the solvent. The amount of bibenzyl necessary to initiate significant amounts of demethylation is quite large. Little effect was detected for solutions of up to 3% bibenzyl in methylnaphthalene, but naphthalene yields became significant when bibenzyl concentrations were increased from 20% to 50%. Thus, the length of the chain of reactions leading to demethylation must be quite short, indicating that termination reactions of the chain carriers must

be quite efficient. Similar factors are undoubtedly important in determining the extent of methane gas formation during coal liquefaction.

Preliminary work has begun on experiments designed to study the chemistry of free radicals immobilized on the surface of a silica support. Immobilized radicals will be used in later work to study hydrogen transfer reactions and rearrangement reactions in the absence of competition from recombination reactions. Phenolic compounds have been bound to the silica surface by heating the components under an inert atmosphere. Thus phenol, 1-(4-hydroxyphenyl)-2-phenylethane, and mixtures of both phenols have been bound to a high-surface-area silica. The phenols may be released quantitatively from the surface by hydrolysis in aqueous base and recovered for analysis. Surface coverages of about 0.6 mmol/g have been achieved. Pyrolysis of the phenylethanephene-derivatized silica has been carried out under vacuum. Product analysis of the volatile material and the organic residues remaining on the surface indicate that the anticipated cleavage of the ethane bridge does take place. Methods to study the radicals generated on the surface by pyrolysis are now being developed.

In the next quarter, the selectivity of demethylation by hydrogen atom attack will be determined by comparing the reactivity of 1- and 2-methylnaphthalene. Work on the study of immobilized radicals will continue with attempts to isolate reactive radicals from each other by bonding along with the radical precursors a large excess of an inert phenol, such as pentafluorophenol.

Fundamental Studies of Coal Liquefaction

B.R. Utz, Cost Account Manager

*B.D. Blaustein, Chief,
Process Sciences Branch*

The objectives of this project are to (1) examine the initial reactions during coal liquefaction by isolating and characterizing the initial dissolution products, primary preasphaltenes, using previously developed techniques, and by isolating and characterizing subsequent hydroliquefaction reaction products involving primary preasphaltenes as a reactant, and (2) examine and quantify the extent of vehicle incorporation under a variety of reaction conditions in order to understand the fate of vehicle components during coal liquefaction. Synthetic vehicles will be used for all experiments.

During this quarter, the extent of vehicle incorporation under a variety of coal-liquefaction reaction conditions was further examined. Earlier studies, using synthetic vehicles, demonstrated that significant quantities of vehicle, tested under Short Contact Time Liquefaction (SCTL) conditions, can be incorporated into coal-derived moieties. This study also demonstrates that specific components of the synthetic vehicle are preferentially incorporated. Understanding what type of conditions enhance vehicle incorporation and what conditions allow ultimate recovery of vehicle is important to a better understanding of coal liquefaction.

The original hypothesis regarding vehicle incorporation in SCTL was that rapid heat-up enhanced vehicle incorporation because the rapid increase in free-radical concentration caused free-radical addition and substitution reactions with components of the vehicle; in addition to the traditionally proposed mechanism of free-radical capping with a source of hydrogen (H_2 or hydroaromatics). The hypothesis was tested by quantifying the extent of vehicle incorporation using three sets of reaction conditions that differed in heat-up rate and time at the reaction temperature of 425°C. The first set of reaction conditions represented a rapid heat-up mode, as in SCTL, to 425°C ($\cong 1$ min heat-up) and 0-30 min at 425°C. The second set of reaction conditions involved a gradual heat-up to 425°C ($\cong 52$ -54 min) and 0-30 min at 425°C, while the third set involved a very slow heat-up to 425°C (375-390 min) and 0-30 min at 425°C. Kentucky 9/14 coal and a synthetic vehicle consisting of 20% tetralin, 20% phenanthrene, 10% pyrene, 13% m-cresol, 4% quinoline, and 33% 1-methylnaphthalene were used.

Heat-up rate, time at reaction temperature (425°C), and time above 350°C were used to evaluate vehicle incorporation. Solubility characterization was used to evaluate the quality of the coal-derived products. The results showed that a rapid heat-up versus a gradual heat-up gave comparable vehicle incorporation values of 5% to 9%, with reaction times above 350°C of 1 to 45 min. The reactions involving a very slow heat-up resulted in greater vehicle incorporation (14% to 17%), with reaction times of 220 to 250 min above 350°C. These results imply that the heat-up mode does not influence vehicle incorporation but that time at temperatures above 350°C may be more important.

It was expected that longer reaction times would not only thermally upgrade coal-derived products but also increase the recovery of vehicle

(less incorporation), since more coal-solvent bonds would be cleaved as the reaction times increased. While the relative amount of toluene-soluble products increased with increasing reaction times, the extent of vehicle incorporation also unexpectedly increased, implying that a greater amount of coal-solvent adduct was forming. At some stage of liquefaction, the coal-solvent bonds should be broken, allowing greater vehicle recovery. To test the limits of this theory, reaction times at 425°C were extended to 6 hours using the gradual heat-up method. Under these conditions, recovery of vehicle components, or components similar in structure to the vehicle, should occur. Although as much as 65% of the coal was converted to cyclohexane-soluble material, the extent of vehicle incorporation was considerably greater than that observed at shorter reaction times. Vehicle incorporation increased from 5% at 0 time, to 7% after 1/4 hr, to 9% after 1/2 hr, and to 29% after 6 hr. These results further demonstrate the formation of coal-solvent adducts and show that the coal-solvent bond is stronger than many of the bonds initially present in the coal matrix. These results imply irreversible incorporation of solvent into coal fragments.

Fundamentals of Coal Liquefaction in the Presence of Water

*H.R. Appell, Cost Account Manager
B.D. Blaustein, Chief,
Process Sciences Branch*

The objective of this project is to explore the basic chemistry of liquefying coal in the presence of water, especially under supercritical conditions, for the purpose of converting the coal to a product suitable for further upgrading to liquid fuels at the lowest possible cost. This study will include investigations of water-stable catalysts that can transfer hydrogen to coal from water or CO/water systems.

The liquefaction of bituminous coals was studied with the objectives of determining conditions under which liquefaction proceeded readily in the presence of water and also for evaluating the relative importance of the processing parameters when water was present as a major component.

The first three tests in Table 15 show that if the coal/water ratio is held constant and the amount of oil (SRC heavy distillate) decreased, the conversion decreases. (Conversion is defined here as 100% THF insolubles.) This result is consistent with well-established data on the beneficial effect of the slurry oil on coal liquefaction. The new fin-

Table 15.
Liquefaction of Illinois No. 6 in the Presence of Water
(42 mL Autoclave, 4 g Coal, 60 min at Temperature)

Test No.	1	2	3	4	5	6	7	8
Oil, g	2	1	0	1.6	1.3	1.6	1.3	1.3
Water, g	1.7	1.7	1.7	1.7	1.7	0	1.7	1.7
H ₂ , psig, cold	1200	1200	1200	800	800	800	1200	1200
Temperature, °C	427	427	427	370	370	370	370	370
(NH ₄) ₂ MoO ₄ , g	0	0	0	0	0	0	0	0.02
Conversion, %	87	78	62	80	61	55	81	90

Note: Conversion = 100% THF insolubles.

ding is that if water is present, it is possible to go to very low ratios of oil to coal before significant drops in conversion occur. All of the oil-to-coal ratios used in this study are significantly less than are normally considered workable in coal liquefaction. It thus appears that a considerable fraction of the slurry oil can be replaced by water before the conversion shows a significant decrease. Furthermore, operation where the total vehicle (oil plus water)-to-coal ratio is less than normal appears possible. The data suggest that the total vehicle-to-coal ratio is an important variable that can be less than conventional oil-to-coal ratios but that, nevertheless, should not go below an as-yet-undefined minimum.

When 4.0 g of Illinois No. 6 coal (River King) was liquefied at 370°C for 1 hour in the presence of 1.6 g of oil and 1.7 g of water, a conversion of 80% was obtained. If the water was omitted, the conversion dropped to 55% (Tests 4 and 6, Table 15).

At the low ratios of oil to coal used in this investigation, the hydrogen pressure is an important variable and has a relatively large effect on the conversion. Attempts to reduce the oil from 1.6 g to 1.3 g resulted in a decrease in conversion

from 80% to 61% at an initial hydrogen pressure of 800 psig. Increasing the initial hydrogen pressure to 1200 psig resulted in an increase in conversion to 81% when liquefaction with the 1.3 g of oil was again attempted. The addition of 0.02 g of ammonium molybdate increased the conversion to 90% when using 1200 psig hydrogen with 1.3 g of oil.

Experiments in which the reaction time was decreased from 60 to 30 minutes showed a decrease in conversion from 81% to 71%-73% (Tests 7, Table 15; and Tests 11 and 12, Table 16). This decrease could be more than compensated for by the addition of small quantities of ammonium molybdate. The addition of 0.25% and 0.5% of ammonium molybdate (based on coal weight) results in conversions of 92% and 97%, respectively. The effectiveness of these small quantities of catalyst suggests that the water may assist in obtaining a good catalyst distribution. Two tests with Kentucky 9/14 coal (Tests 9 and 10, Table 16) indicate a reactivity close to that of Illinois No. 6 in the absence of added catalyst but significantly less reactivity when compared in the presence of ammonium molybdate.

Table 16.
Effect of Coal in the Liquefaction in the Presence of Water
(42 mL Microautoclave, 4 g Coal, 1200 psig H₂, 370°C, 30 minutes)

Test No.	9	10	11	12	13	14
Coal	KY 9/14	KY 9/14	III. #6	III. #6	III. #6.	III. #6.
Oil, g	1.45	1.45	1.3	1.3	1.3	1.3
Water, g	1.7	1.7	1.7	1.7	1.7	1.7
(NH ₄) ₂ MoO ₄ , g	0	0.01	0	0	0.01	0.02
Conversion, %	73	78	71	73	92	97

Note: Conversion = 100% THF insolubles.

AR&TD: ENVIRONMENTAL ASPECTS OF FOSSIL FUEL COMBUSTION

B.D. Blaustein, Coordinator

The objectives of these two projects are to support FE/HQ in their activities as chair of Task Group B — Man-Made Sources, which is part of the Federal Interagency Task Force on Acid Rain Precipitation.

During this quarter, further results on the Acid Precipitation Studies project have been reported by the National Bureau of Standards on the potential of new isotopic tracer and trace element analytical methodology for acid-rain-related studies. In addition, analyses are being carried out on aerosol samples that were collected as part of the Deep Creek Lake Experiment. A draft final report was received from the Department of Atmospheric and Oceanic Science of the University of Michigan that describes the calculated back trajectory meteorological data for the Deep Creek Lake Experiment.

In the Acid Rain Precursor Studies project, several more sulfate emissions factors' tests were run on the 700-hp boiler. A preliminary review of the data suggests that the levels of sulfate found were commensurate with the level formed from flame chemistry alone. A field testing program may be necessary to complete the required sulfate data. Testing for chloride and fluoride emissions continued.

Acid Precipitation Studies

Y.S. Pan, Cost Account Manager

**B.D. Blaustein, Chief,
Process Sciences Branch**

The objective of this project is to support FE/HQ in their activities in Task Group B — Man-Made Sources, which is part of the Interagency Task Force on Acid Precipitation.

Under an interagency agreement between the National Bureau of Standards (NBS) and the Pittsburgh Energy Technology Center (PETC), the NBS is performing a literature survey to identify and assess the potential of isotopic tracers for coal emissions, measuring sulfur isotope ratios in selected samples from the Deep Creek Lake Experiment, and examining the feasibility of using new isotopic tracer and trace element technology for acid-rain-related studies. During this reporting period, the following accomplishments were reported.

- a. A detailed study of the use of enriched stable isotopes of the rare earth elements as tracers of aerosol emissions from coal-fired power plants has been completed. A proposal that details a definitive method of tracing aerosol

from a point or regional source to a receptor site was prepared by W.R. Kelly of NBS and J.M. Ondov of Martin-Marietta, and submitted to EPRI and DOE.

- b. Preliminary calculations have been completed on the use of enriched ^{36}S as an intentional tracer of sulfur compounds. An invitation was extended to W.R. Kelly to talk on this topic at DOE Headquarters and at the Council on Environmental Quality, Washington, D.C.
- c. One of the elements that is enriched in coal relative to other rocks is boron. A preliminary literature investigation on the possible use of the $^{10}\text{B}/^{11}\text{B}$ ratio to trace emissions from coal-fired power plants has been completed. At the present time, there are no isotopic data on boron in coal. The objective of this task is to measure the $^{10}\text{B}/^{11}\text{B}$ ratio and the B/S ratio in coals and aerosol samples. This may enable one to determine that portion of an aerosol that is derived from coal combustion.

The objectives of a contract with the Martin-Marietta Corporation are to perform studies on submicrometer aerosols to provide an independent analysis of source contributions and to differentiate the impacts of near and distant sources, and to obtain chemical composition profiles of submicrometer particles needed from the receptor site and for the sources. The samples collected with the micro-orifice impactor (MOI) as reported in the last quarterly report were delivered to the U.S. Environmental Protection Agency's (EPA) Environmental Sciences Research Laboratory (ESRL) for elemental analyses by X-ray fluorescence (XRF).

A report on the use of an airborne platform for aerosol sampling, by the Virginia Polytechnic Institute and State University, has just been completed. Two regional background sampling flights of nine hours each were carried out over the Wayne National Forest in Eastern Ohio. One aerosol sampling run was carried out at the Kraft Paper Mill in Chillicothe, Ohio, and two aerosol sampling flights were conducted in power plant plumes in West Virginia. Emissions at the Harrison West Virginia Power Station are controlled with precipitators, while at the Pleasants Power Station, they are controlled with an electrostatic precipitator and a scrubber. A micro-orifice impactor furnished by V.A. Marple of the University of Minnesota, under contract with PETC, and a Teflon cyclone extraction impactor unit furnished

by R.K. Stevens of EPA/ESRL were both operated during these sampling flights. All samples have been delivered to EPA/ESRL for elemental analyses by XRF.

The project with the Department of Atmospheric and Oceanic Science, University of Michigan, was conducted during the summer of 1983 to forecast weather conditions at the sampling site at Deep Creek Lake, McHenry, Md., and to help quantify the atmospheric transport processes occurring over middle-scale or "meso-scale" distances in the upwind region of the site. Using on-line computer capabilities, the wind speed, wind direction, temperature, humidity, precipitation, and cloud-cover data reported by the National Weather Service (NWS) within about 500 km of the study site were made available each morning and as required by project participants. Additionally, upper-air data from nearby NWS stations were also collected daily and stored at the site. At the end of the study period, the data were returned to the University of Michigan, where they have been archived and stored on magnetic tape. Back trajectories (the most probable path followed by the sampled air enroute to the receptor) have been computed for all the days in the study period using the available surface-based and upper-air data collected during the study period. Trajectories were calculated for the 850-mb level (roughly 1500 meters above mean sea level) using upper-air-wind observations taken twice daily (0800 and 2000 EDT) at the nine selected NWS radiosonde stations. The trajectories were computed upwind to estimate the location of the air at 850 mb up to 48 hours prior to its arrival at the sampling point. Trajectories were also calculated using surface level wind observations taken hourly at all NWS stations within a 500-km radius of the Deep Creek Lake monitoring site. The results of the trajectory calculations for the surface and 850-mb level are contained in the draft of the final report, which is being reviewed.

Acid Rain Precursor Studies

J.M. Ekmann, Cost Account Manager

J.I. Joubert, Chief,

Combustion Technology Branch

The objective of this project is to determine factors for sulfate emissions from oil-fired package boilers representative of the residential and commercial market, and for chloride and fluoride emissions from industrial coal combustion. These emission factors will be developed from test data taken during combustion tests at PETC.

During the past quarter, several more sulfate tests were run on the 700-hp boiler. In addition, the available data were reviewed. This preliminary review suggests that our measurements were finding levels of sulfate commensurate with the level formed from flame chemistry alone. This finding is reasonable given the level of maintenance and cleaning that these boilers receive.

Chloride and fluoride testing continued. Data from these tests will be reviewed to see if further testing is required.

The sulfate results indicate that a field testing program may be necessary to complete the required sulfate data. Only limited additional testing is planned in-house during the last quarter, primarily for quality assurance purposes.

COAL PREPARATION

A.W. Deurbrouck, Coordinator

Initial float-sink testing on minus 325 mesh coal has provided suspect data. Impurity release upon crushing to this fine size has been minimal, and in a number of cases, the recovery at a given specific gravity has actually decreased. To correct this problem, a series of tests is being conducted in which the samples of fine size coal are being pretreated in an attempt to make them more responsive to float-sink testing.

Collection, assembly, and preparation of the pyrite particle size distribution data for statistical analysis and arrangement into an acceptable form for reporting have begun. Preliminary data figures are included.

Final results for a 48-test series on procedural reproducibility of selective coalescence tests proved to be positive. Our in-house sample reserve now contains three samples, with two additional samples expected within the next month. We anticipate that by the end of August we will have the full complement of ten coals in reserve.

Laboratory froth flotation tests were conducted with dry- and wet-ground coal to determine the effect of grinding methods on clean coal recovery and product ash content. The test results showed that the dry-ground coal is more floatable, but the wet-ground coal provided substantially lower ash products at equivalent yields.

Work continued on the binder developed by W.W. Wen. An investigation of the influence of binder shelf life on coal pellets' strength and durability revealed some deterioration of agglomerant strength characteristics, but the values obtained still appear to fall in an acceptable range. Pellet abrasion tests were performed to assess the quantity of fines that might be generated in the course of normal material-handling operations. Using the customary test procedure for determining the amount of fines

produced, an abrasion strength of 95% to 99% was obtained for bituminous coal pellets. These values were quite high when compared with the results reported in the literature.

In experiments using microreactors, it has been observed that at 370°C, benzothiophene reacts with molten alkali metal hydroxides to form a variety of products. Total conversion to other products appears to be high, of the order of 70% in one hour. Many of the products are water soluble. A principal product of the reaction is tentatively identified as o-cresol. In addition, a higher molecular weight sulfur-containing species, perhaps a dimeric product, has been observed in the gas chromatogram. This reaction is the first example of a model compound representative of the types of structures believed to exist in coal that reacts with NaOH/KOH to lose sulfur.

Fine Coal Characterization

J.A. Cavallaro, Cost Account Manager

***A.W. Deurbrouck, Chief,
Coal Preparation Branch***

The objective of this study is to determine the effects of crushing coal on the liberation of ash, pyritic sulfur, and other impurities, and the subsequent reduction potential of these impurities upon gravimetric separation.

This quarter, testing continued in an attempt to resolve the yield/ash relationship anomalies that have appeared in the float 1.30 specific gravity fraction of the 200 mesh by zero and 325 mesh by zero size fractions. Gravimetric tests were conducted using hexametaphosphate to neutralize the effects of clay slimes coating the clean coal particles and aerosol as a dispersant. Results showed an improvement in the yield and ash contents of the float 1.30 specific gravity product. The yield increased slightly (0.4 percentage points)

and the ash content decreased 0.4 percentage points using hexametaphosphate, while the yield increased 3.9 percentage points and the ash decreased 0.3 percentage points using aerosol OT-100. Reverse float-sink technologies, i.e., separating in the order of 1.60, 1.40, and 1.30 specific gravities, provided a product of 27.0 wt% recovery at a 2.7% ash content. These data are shown in Table 17.

Thus, the use of various surfactants and float-sink techniques showed improvements in the weight recoveries and ash contents of the float 1.30 specific gravity product.

Additional tests were conducted by preheating a raw coal sample of Lower Kittanning bed coal from Webster County, W.Va., and adding a surface-active agent. The intent was to determine the effects of the removal of the inherent moisture and the addition of a dispersant prior to float-sink testing. This resulted in a significant increase in the weight recovery of the float 1.30 specific gravity fraction (18.0% to 29.3%) and a decrease in ash content for each of the other specific gravity fractions. The data are tabulated in Table 18.

The washability data for this coal when crushed from 1 1/2 inches top size down to 44 microns is presented in Figure 6 and shows the improvement achieved in the yield-ash relationship when preheating the sample and using aerosol as a

dispersant. We feel that this is a significant step in the right direction; however, additional tests are being conducted to establish reproducibility and optimal results.

Figure 6 -

Table 17.
Upper Kittanning Bed Coal, Monongalia County, W.Va.

Cumulative Data, %

	Normal F-S		Reverse F-S		Hexametaphosphate		Aerosol OT-100	
	wt	ash	wt	ash	wt	ash	wt	ash
Float 1.30	25.4	3.3	29.3	3.0	25.8	2.9	27.0	2.7

Table 18.

Cumulative Data, %

	Original Sample		Preheat Sample Plus Aerosol	
	wt%	ash%	wt%	ash%
Float 1.30	18.0	3.4	29.3	3.0
1.30 x 1.40	45.7	5.9	49.3	4.7
1.40 x 1.60	66.1	9.2	65.8	7.7
Sink 1.60	100.0	25.9	100.0	24.9

Pyrite Particle Size Distribution

J.E. Puskas, Cost Account Manager

*A.W. Deurbrouck, Chief,
Coal Preparation Branch*

Substantial progress has been made this quarter. The pyrite particle size measurements on the Quantimet 720 have proceeded smoothly in the last two months. Analyses on the 14 mesh by zero and 325 mesh by zero raw coal, 1.40 specific gravity float and 1.40 specific gravity sink fractions have been completed for the 13 coals of the Northern Appalachian Region. Maceral component determinations of the 325 mesh top size raw coal and the 1.40 specific gravity float and sink fractions are continuing. This work will be completed in the next quarter.

One remaining determination must be initiated for the 13 coals — the degree of pyrite liberation for each of the crushed coal sizes and gravimetric fractions. These microscopic evaluations have been delayed so that a standard laboratory procedure could be established in discussions with petrographer Ralph Gray, who came on-board this quarter.

Collection, assembly, and preparation of the data for statistical analysis and arrangement into

a logical form for reporting has begun. Some of the preliminary data were reported last quarter. Attached are some additional preliminary data for coals that have been completed.

Figures 7 through 12 are graphs of pyrite particle size (diameter in microns) versus number of particles, for both 14 mesh by zero and 325 mesh by zero sizes of three different coals. In general, these graphs show that most of the samples represented by the figures have pyrite particle size distributions that obey the log normal function (Gaussian distribution). Also, each of the components of a coal bed sample group, which consists of the raw coal and the float and sink fractions from the 1.40 specific gravity gravimetric analysis, are generally well-defined and right-skewed, showing the natural relationship between the pyrite size distribution of the clean coal (float materials) and the refuse (sink materials).

Table 19 presents a summary of the pyrite size data generated by the image analysis system and compares it to the pyritic sulfur reduction potential obtained from the washability analysis. The most important observation from this table, and the goal of the project, is the relationship of the coal particle size to the pyritic sulfur reduction. It

Figure 7- Pyrite Distribution

Figure 8- Pyrite Distribution

Figure 9- Pyrite Distribution

Figure 10- Pyrite Distribution

Figure 11- Pyrite Distribution

Figure 12- Pyrite Distribution

Table 19.
Correlation of Pyrite Particle Size with Pyritic Sulfur Reduction

Product	Top Size, Mesh	Average Pyrite Diameters, Microns			Pyritic Sulfur, Percent		
		Mean	Volume Mean	Weight Mean	Content	Reduction	Free ^b
PITTSBURGH BED COAL, JEFFERSON COUNTY, OHIO ^a							
Raw	14 x 0	4.47	8.86	27.57	2.25	—	20.1
Float 1.40	14 x 0	4.76	8.00	22.79	0.89	60.4	6.4
Sink 1.40	14 x 0	4.77	9.52	28.24	5.33	—	32.4
Raw	325 x 0	4.27	7.32	18.65	2.20	—	77.0
Float 1.40	325 x 0	3.23	4.61	12.15	0.23	89.5	35.0
Sink 1.40	325 x 0	4.72	7.79	18.07	6.61	—	83.4
PITTSBURGH BED COAL, WESTERMORELAND COUNTY, PA							
Raw	14 x 0	3.76	6.25	18.78	0.20	—	— ^c
Float 1.40	14 x 0	3.50	4.81	9.01	0.15	25.0	—
Sink 1.40	14 x 0	4.51	6.16	24.67	—	—	—
Raw	325 x 0	4.11	7.96	25.77	0.19	—	—
Float 1.40	325 x 0	3.68	5.06	8.63	0.08	57.9	—
Sink 1.40	325 x 0	5.70	10.27	26.57	—	—	—
PITTSBURGH BED COAL, ARMSTRONG COUNTY, PA							
Raw	14 x 0	4.94	7.40	16.74	1.25	—	—
Float 1.40	14 x 0	5.46	7.51	14.21	0.76	39.2	—
Sink 1.40	14 x 0	5.40	7.82	17.72	2.00	—	—
Raw	325 x 0	4.71	7.42	19.30	1.26	—	—
Float 1.40	325 x 0	4.32	5.34	8.08	0.21	83.3	—
Sink 1.40	325 x 0	4.25	6.93	21.61	2.55	—	—

^aPreliminary data

^bManually observed particle counts

^cNot yet determined

is also interesting to note the relationship between pyritic sulfur reduction and percent free pyrite.

Maceral analysis, microscopic determination of the free pyrite and degree of association of pyrite in the selected crushed-coal sizes, and data compilation will continue next quarter.

Selective Coalescence

C.P. Maronde, Cost Account Manager

*A.W. Deurbrouck, Chief,
Coal Preparation Branch*

The objective of this project is to investigate and accelerate the development of selective coalescence processes for cleaning ultrafine coal to low ash levels. Testing is being done on a laboratory scale in a batch mode and consists of three interrelated tasks: (1) development of in-house expertise, (2) verification and comparison of new selective coalescence technologies, and (3) advancement of the state-of-the-art.

Due to the Branch reorganization, this project is in a transition period. We will be wrapping up each of the tasks previously described within the next 1 to 2 months. The technicians previously assigned to this project have been detailed to other projects. However, as the work load permits some final wrap-up laboratory experimentation will be conducted. Also, as part of the reorganization, Carl Maronde has been assigned as the cost account manager for this project.

Compilation of the bibliography continued. A rough draft will be completed by the end of next month.

Final results for the 48-test series on procedural reproducibility were received. Three technicians each ran an identical series of tests four times. Results showed excellent reproducibility by two of the operators and just slightly less by the third. (The range of clean coal ash variability as a percent of the average ash for operator A was 3%, for B, 6%, and for C, 10%.)

Preliminary results on the effect of kerosene addition level on product ash and weight recovery show that it is possible to realize modest ash reductions even with the addition of only 1% kerosene; however, recovery of material is sacrificed. It appears that little improvement in separation is seen when the kerosene addition level exceeds the 5% to 7% range. Also, selection of the proper screen-opening size plays an important role in the final product quality and quantity.

A report on the laboratory experimentation thus far completed is in preparation.

Our in-house sample reserve now contains three samples, and two additional samples are expected within the next month. We anticipate that by the end of August, we will have the full complement of 10 coals in the reserve — 1 anthracite, 6 bituminous, 2 subbituminous, and 1 lignite. Samples for the reserve were chosen on the basis of seam characteristics, reserve data, and present production statistics. A description of the storage system and handling procedures is being written.

Plans for the round-robin comparison of selective coalescence technologies have been made final. Official invitations to participate in the project will be mailed out shortly.

Flotation and Dewatering

K.J. Miller, Cost Account Manager

*A.W. Deurbrouck, Chief,
Coal Preparation Branch*

This project consists of two major tasks, froth flotation and mechanical dewatering. The objective is to develop methods that will more selectively reject mineral matter from ultrafine coal and to improve the efficiency of mechanical dewatering of the cleaned-coal product and the fine refuse.

A. Flotation

Laboratory froth flotation tests were conducted with dry- and wet-ground coal to determine the effect of grinding methods on clean-coal recovery and product-ash content. Dry grinding was done in a laboratory air-classifying impact mill, and wet grinding was done in a stirred ball mill and in a conventional ball mill with a medium of 3/16-inch stainless steel balls. Products of as near the same size as possible were prepared by each method, i.e., nominal minus 27 micrometers with a mean particle size of 10 to 12 micrometers.

The test results obtained to date show that the dry-ground coal is more floatable (i.e., greater wt% recoveries were obtained at any given reagent dosage), but the wet-ground coal provided substantially lower ash products at equivalent yield. For example, the dry-ground coal yielded about 20 wt% to over 80 wt% froth product with frother addition levels of 0.1 to 0.5 pound per ton of dry coal (lb/ton), respectively, and the product ash contents ranged from 2.0% to 4.0%. The wet-ground coal, on the other hand, yielded about 25 wt% to a little over 70 wt% with froth addition

levels of 0.2 to 0.5 lb/ton, and the product ash ranged from 1.5% to 2.0%. The feed or raw coal contained about 5.0% ash.

B. Dewatering

A detailed evaluation of a laboratory cyclone test rig was completed, and the data were evaluated and compiled. The test rig was operated with a one-inch and a two-inch classifying cyclone, each with various vortex finders and underflow orifices. The data show the degree of classifying, or desliming, possible with the test rig under a wide variety of operating conditions. The information is necessary in order to test various degrees of desliming prior to dewatering by vacuum filtration or centrifugation.

Fine-Size Coal Agglomeration

P.D. Bergman, Cost Account Manager

*A.W. Deurbrouck, Chief,
Coal Preparation Branch*

The objective of this project is to provide, by means of agglomeration procedures, a technically and economically viable method for delivery of deep-cleaned fine coal to potential consumer markets in a commercially usable form. The agglomerated material must be resistant to dusting, weathering, mechanical abuse, and spontaneous combustion, as well as having a low-moisture content and high-heating value. Once the low-ash, low-sulfur coal pellets are delivered, they may be directly burnt, pulverized and then burnt, or employed as a feedstock for slurry fuel production, depending upon the contemplated user application. Thus, agglomeration represents a simple, easily implemented technique for transporting high-quality solid fuel to users interested in substituting coal for oil and natural gas in new or retrofit combustion situations.

Previous cost analyses indicated that the binder cost represented approximately 40% to 50% of the total pelletization plant operating costs. In order to reduce the binder expense, we have developed a low-cost coal-derived organic binder, which has been utilized successfully to produce weather-resistant, high-strength, readily transportable coal pellets. A patent application detailing these findings is being prepared.

An investigation of the influence of binder shelf life on coal pellet strength and durability revealed some deterioration of agglomerate strength characteristics, but the values obtained still appear to fall in an acceptable range for railroad transportation and delivery of the final enlarged product.

The effects of this phenomenon were studied after two weeks of binder aging, which is well beyond the maximum shelf life anticipated for large-scale industrial production of coal pellets and briquettes. Two independent tests indicate that binder aging, although it could constitute a serious research problem, will not have a major impact in the operation of a commercial pelletization facility. A representative set of coal pellets was immersed in water for several weeks without being dissolved. However, the pellet compressive strength and impact strength were degraded well below the acceptable limits for coal handling and storage.

Pellet abrasion tests were performed to assess the quantity of fines that might be generated in the course of normal material-handling operations. Using the customary test procedure for determining the amount of -48 mesh fines produced as a result of rapid vibration in a ball mill jar, an abrasion strength of 95% to 99% was obtained for bituminous pellets produced in four previous tests. These values were quite high when compared with results reported in the literature for other common binder systems.

In order to more carefully monitor the binder preparation and pelletization process, an analytical procedure for measuring the extent of oxidation of various coals and binder mixtures has been applied successfully. Solubility in sodium hydroxide solution serves as a measure of the degree of coal oxidation present. This analytical technique may eventually serve as a measure of binder activity, particularly with reference to organic binders prepared in the laboratory from coals other than lignite. This line of inquiry will be pursued in the next fiscal year. The Analytical Chemistry Branch is presently attempting to use various spectroscopic and optical absorption techniques to elucidate the chemical structure of the PETC binder.

Chemical Coal Cleaning Studies

S. Friedman, Cost Account Manager

*B.D. Blaustein, Chief,
Process Sciences Branch*

The objectives of this work are to investigate the chemistry of sulfur in coal so that economic methods can be developed to desulfurize coal using chemical methods. Effective pretreatment of coal to remove most of the sulfur prior to combustion could be an important technology for control of sulfur dioxide emissions from coal combustion. Although several chemical desulfurization processes are under active development in vari-

ous laboratories and are being monitored, little is known about the chemistry of sulfur in coal, and thus there is scant understanding of the mechanisms that control the chemical removal of sulfur from coal. Work on this project is intended to increase our understanding of the basis for chemical desulfurization of coal, as well as to devise new ways to desulfurize coal.

In the previous quarterly report, it was indicated that dibenzothiophene was inert to molten NaOH/KOH at 390°C, and this has been confirmed in a second experiment. Since up to 80% of the organic sulfur in some coals is reported to be removed by these reaction conditions, it appears that much organic sulfur in coal must be present in some form other than dibenzothiophenic groups. In experiments using microreactors, it has now been observed that even at 370°C, benzothiophene reacts with molten alkali metal hydroxides to form a variety of products. Total conversion to other products appears to be high, of the order of 70% in one hour. Many of the products are water soluble, necessitating repeated extraction of the aqueous work-up solution. A principal product of the reaction is tentatively identified as o-cresol. In addition, a higher molecular weight sulfur-containing species, perhaps a dimeric product, has been observed in the gas chromatogram. In one experiment, because of poor mixing of the benzothiophene and the molten alkali, no reaction occurred, demonstrating how dependent this type of heterogeneous, two-phase reaction can be with respect to efficient mixing.

This reaction is the first example of a model compound representative of the types of structures believed to exist in coal that reacts with NaOH/KOH to lose sulfur. In the model system, there is also the loss of a carbon atom for each sulfur atom removed. It has already been demonstrated in earlier work done at the PETC that if the sulfur, even in dibenzothiophene, is oxidized to the sulfone, it can be removed readily by alkali metal hydroxides at 300°C. The possibility of preoxidation of the resistant sulfur in coal to make it more amenable to alkali treatment will be re-examined in light of the current interest in molten alkali treatment of coal.

Further work in this area will include extending this reaction to polymeric materials. Polymers have been prepared from phenyl vinyl sulfone and phenyl vinyl sulfoxide using standard free-radical polymerization techniques. These high-melting polymers are being characterized by FTIR and NMR. They are both expected to have a long aliphatic chain (polyethylene type) to which is appended, at every other carbon atom, a sulfoxide or sulfone group to which is attached a phenyl group. These polymers will be used for calibrating the controlled-temperature oxidation apparatus. In addition, they will be used as starting materials for preparing a polyphenyl alkyl sulfide with a long alkyl-chain backbone. This material will be particularly useful in experiments with molten alkali hydroxides. Other types of polymers containing aryl and alkyl sulfide linkages are being prepared, both for oxidation behavior studies and for molten alkali treatment.

UTILIZATION: COAL COMBUSTION CLEANUP TECHNOLOGY

C.J. Drummond, Coordinator

This program is directed toward the development of advanced environmental control technology for coal-fired stationary sources, and the determination of the potential hazard of related wastes after disposal. Studies include the parametric evaluation of processes providing simultaneous removal of SO₂, NO_x, and particulates from the flue gas of coal-fired boilers, and the development of an analytical methodology for the analysis of organic constituents in leachates.

During this quarter, testing of the PETC Fluidized-Bed Copper Oxide Process continued. A 3-inch-diameter slide-gate valve was installed in

the copper oxide sorbent hopper replacing a rotary-air-lock feeder used in previous studies. This modification of the system significantly reduced the sorbent attrition rates observed.

Cooperative tests with Wheelabrator-Frye, Inc. (WFI) on the 500 lb/hr Solid-Fuel Combustion Test Facility to determine the particulate control efficiency of an electrostatic precipitator (ESP) while operating a spray dryer for sulfur dioxide control have been completed.

The facility for continuous life-cycle testing of the copper oxide sorbent is in the final stages of design. Design of this unit includes a pulverized-

coal-fired furnace capable of firing at a rate of 40 lb/hr. Several modifications have been made to the initial process design in order to minimize sorbent attrition and more accurately measure material flow. Construction of this facility began this quarter.

Construction of the dry combined flue gas cleanup facility is complete. A program is underway to establish the various operational ranges of this unit and to correct any deficiencies in the system.

Sulfur dioxide absorption tests continued in the microbalance reactor with various preparations of copper oxide powder. Results showed that 40% to 60% utilization of the copper oxide powder was achieved.

To determine the potential application of advanced separation technology to flue gas cleanup, fourteen processes that involve wet simultaneous NO_x/SO_2 removal that have reached larger than bench-scale application were evaluated and summarized.

In the evaluation of the Lurie Process, titration curves for sodium aluminate and sulfuric acid are being developed to simulate the sulfur absorption chemistry of this process.

As a part of the Fossil Energy Technology Waste Sampling and Characterization Program, the analytical method entitled "Proposed Method for the Determination of Semi-Volatile Organic Compounds in Aqueous Leachates of Wastes," ASTM document 34.03-010, is being submitted for round-robin testing.

Flue Gas Cleanup

J.T. Yeh, Cost Account Manager

J.I. Joubert, Chief,

Combustion Technology Branch

Proof-of-Concept Testing

During FY83, a project involving simultaneous removal of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) via a fluidized-bed copper oxide process was conducted. The results of the project were generally successful; however, physical attrition losses of the copper oxide sorbent employed were somewhat higher than found in earlier PDU tests of the process. In further testing of the copper oxide process in FY84, an attempt is being made to identify the causes of sorbent attrition, and approaches to correcting the problem are being identified. These tests are being conducted in the 500 lb/hr Solid-Fuel Combustion

Test Facility at PETC. Interwoven with these tests is a series of three spray dryer/ESP tests conducted in cooperation with Wheelabrator-Frye, Inc. (WFI).

A. Fluidized-Bed Copper Oxide Process

A 3-inch-diameter slide-gate valve was installed in the copper oxide sorbent hopper to control the flow rate of sorbent into the fluidized bed. A test was made using the control valve during a coal combustion flue gas cleanup test. Sorbent particles smaller than 20 mesh were screened and removed before operation of the fluidized-bed for simultaneous SO_2/NO_x removal. Attrition based on sorbent carry-over to the baghouse was 0.16% per hour of bed inventory; this was significantly lower than attrition rates measured while operating with a rotary-air-lock feeder.

A test was conducted to evaluate the use of methane instead of ammonia in the copper oxide process for the catalytic reduction of nitrogen oxides. During operation of the fluidized-bed, no reduction of NO_x was detected with the injection of methane. Sulfur dioxide concentrations in the flue gas leaving the fluidized-bed absorber increased with increasing quantities of methane injected. It has been suggested that reduction of copper sulfate (to produce sulfur dioxide) occurred before the reduction of nitrogen oxides could take place.

B. PETC/WFI Cooperative Research

The cooperative evaluation of the performance of a pilot electrostatic precipitator (ESP) was completed during this quarter. The last of a series of three tests was completed using a Kentucky coal with high resistivity ash and a 0.7% sulfur content. The data show that the Wheelabrator-Frye Electrostatic precipitator provides excellent particulate control efficiency for this coal while operating a spray dryer for sulfur dioxide removal. Data will be reported for all three series of tests during the next quarter.

C. Attrition Tests Using a 9 1/2-Inch-Diameter Fluidized Bed

Another series of tests was completed on the 9 1/2-inch-diameter fluidized bed to evaluate the effect of fly ash on sorbent attrition. A 36-inch bed of sorbent pellets was fluidized with air, then with air containing fly ash, and the sorbent attrition rates were compared. The latest attrition rates determined were 0.27%/hr/bed inventory with the injection of fly ash, and 0.06% or less when only

air was used. The next series of tests will be conducted at a bubble cap exit velocity of one-third the velocity currently used.

Copper Oxide Process, Continuous Life-Cycle Tests

R.B. Snedden, Cost Account Manager

*J.I. Joubert, Chief,
Combustion Technology Branch*

In addition to the attrition testing in the 500 lb/hr Solid-Fuel Combustion Test Facility, a small-scale (100 scfm) continuous PDU is being designed and constructed to determine the effective life of the sorbent used in the fluidized-bed copper oxide process. A small coal combustion system will supply flue gas to a fluid bed absorber capable of operating continuously. The spent sorbent will be transferred continuously to a moving-bed reactor, where the sorbent will be contacted with reducing gases to produce an SO₂-rich off-gas. The regenerated sorbent will be transferred continuously to the absorber to initiate another cycle.

The reactivity of the sorbent toward SO₂ and NO_x will be monitored over more than one thousand cycles. The effects of trace elements from coal combustion on sorbent chemistry will be examined, and physical attrition of the sorbent will be determined periodically throughout the testing.

Construction of the 40-lb/hr combustor shell started during mid-June. Fabrication of the flue gas exit cone was completed by the machine shop, and a material requisition was submitted to the purchasing office for panel coils to cool the furnace cone bottom. Panel coils for the combustor shell were ordered previously.

Design of the combustor coal feed system is finished. Some materials necessary to build this system have already been ordered. A volumetric screw feeder and an ejector system were obtained from surplus government equipment. Plans are being made to connect the feeder controls and ejector system to test feeder performance. Layout sketches are being prepared for the furnace and coal-feed systems' support structure.

The burner design is complete. Detailed shop drawings will be prepared in order to machine the necessary components for assembly of the burner.

A sorbent transport test loop is being built and will be operated to identify potential sources of sorbent attrition and plugging in the continuous life-cycle test facility. Materials for this test loop

have been received, and construction of the facility has begun. Information on flow control, dense-phase transport, and sorbent attrition will be obtained during the next quarter.

Three gas analysis stations for the continuous life-cycle facility have been designed. All of the required gas analyzers, moisture eliminators, pumps, filters, and valves have been ordered.

A list of long-lead-time equipment for this project was prepared, and several items have been ordered. Surplus equipment is being evaluated for possible use in the process. This would further reduce the number of long-lead-time items required.

Design of the fluid-bed absorber is near completion. Regenerator design will be completed next quarter.

Dry Combined Flue Gas Cleanup Processes (Bench Scale)

R.B. Snedden, Cost Account Manager

*J.I. Joubert, Chief,
Combustion Technology Branch*

Results of recent tests conducted by Niro Atomizer, Inc., and NOXSO Corporation indicate that combined removal of SO₂ and NO_x is possible if "dry" scrubbing processes are operated within a narrow temperature range (100°C to 130°C). Niro utilizes a slurried sorbent containing lime and sodium compounds, and injects the sorbent into the flue gas via a spray dryer; NOXSO employs a fluidized bed of supported sodium oxide on alumina.

In FY84, it is planned to examine other sorbents and sorbent combinations with potential for combined SO₂/NO_x removal. Exploratory tests are being conducted in a laboratory test facility that has been equipped with a small spray dryer (30-inch diameter) and a fabric filter. The candidate sorbents will be evaluated both as dry powders, injected into the flue gas ducting, and as solutions or slurries, injected into the flue gas via the spray dryer. If a suitable temperature "window" can be found that permits high levels of both SO₂ and NO_x removal, this approach could provide a low cost retrofit technology for existing boilers.

Construction of the dry combined flue gas cleanup facility, including the combustor, spray dryer, and gas analysis stations, is complete. During this quarter, shakedown operations were begun. Several problems were discovered during these trial runs. Severe air in-leaks were detected in the flue gas cooler, the rotary spray dryer, and

the baghouse. Air leakage was eliminated in the flue gas cooler and the baghouse by (1) replacement of the flue gas cooler with a double-tube, air-cooled section in the flue gas line, (2) coating all gaskets in the baghouse with high temperature RTV compound, and (3) replacement of the rubber parts of the pulse-air-cleaning connectors in the baghouse. The air leak at the spray dryer occurs through the shaft seal of the rotary atomizer. It appears that this leak cannot be eliminated and must be taken into consideration during data analysis. Another problem observed was an inability to obtain the desired upper temperature levels at the spray-dryer inlet. This was corrected by replacing the water-cooled flue gas pipe at the furnace exit with an air-cooled pipe section.

Several tests were conducted to pinpoint additional operating problems and to gain more experience in operation of the process. Operation of the spray dryer at inlet and outlet temperatures on the low end of the desired range of temperatures (400°F inlet and 180°F outlet) presented a problem. At an outlet temperature of 180°F, moisture condensed on the spray-dryer sight glass. To protect the baghouse, ID fan, and connecting flue gas lines from severe acid corrosion, a reheater was installed after the spray dryer and before the baghouse. Temperatures exceeding the acid dew point can now be maintained throughout the remainder of the flue gas system.

A shakedown program is underway to establish the various operational ranges of the process units. Difficulties have been encountered in slurry handling. Feed lines have been plugged several times due to slurry settling and scaling. Transport lines may be replaced with smaller piping to provide higher velocity slurry flow.

An experimental matrix has been developed for formal testing of sodium aluminate slurry for combined SO₂/NO_x removal in a spray dryer - baghouse unit. Once equipment limitations are established and shakedown is satisfactorily completed, formal tests will be conducted to meet the program objectives.

**Combined Flue Gas Cleanup with
Metal Oxides and Reducing Gases**
D.F. Gyorke, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch

The absorption of SO₂ in the presence of oxygen is thermodynamically favored for nearly all metal oxides at some temperature in the range of 25°C to 800°C. While experimental data on the

kinetics of SO₂ absorption on some metal oxides have been measured, the amount of reported data is limited. Virtually no information is available on the potential catalytic activity of many metal oxides and sulfates with respect to decomposition of NO_x with reducing gases.

During FY84, SO₂ absorption kinetics data will be measured for a number of metal oxides that could potentially be used as sorbents in flue gas cleanup processes. An existing laboratory microbalance reactor is being used for this purpose. A laboratory-scale apparatus will also be constructed to evaluate the catalytic activity of various metal oxides and sulfates in the decomposition of nitrogen oxides in the presence of various reducing gases (e.g., NH₃, CO, H₂, and CH₄).

The sorbents judged to be most promising in the laboratory investigation will be subjected to further testing in the PDU used in the study of Dry Combined Flue Gas Cleanup Processes or in the Solid-Fuel Combustion Test Facility via duct injection upstream of the baghouse filter.

Initial studies of combined flue gas cleanup with metal oxides are being undertaken using unsupported copper oxide. This testing takes advantage of experience drawn from the fluidized-bed copper oxide studies performed on the PETC 500 lb/hr Solid-Fuel Combustion Test Facility as well as other tests of supported copper oxide performed on the PDU and microbalance units. The use of copper oxide powder avoids the costs of the alumina support used in these previous tests.

Construction of the laboratory-scale packed-bed reactor unit has not yet begun due to delays in the remodeling of the room where the unit is to be located. As nearly all necessary equipment and instrumentation for the unit has been delivered, an alternate site will be chosen if the original site is not available soon. A more energetic testing program has been undertaken using the microbalance to compensate for delays in the construction of the laboratory-scale packed-bed reactor.

Results have been analyzed for microbalance tests conducted last quarter on copper oxide powder. Utilization of copper oxide from technical grade powder in absorption tests at 500°C, 550°C, and 600°C was never greater than 8%. Copper oxide prepared by decomposing copper sulfate pentahydrate in a muffle furnace at 800°C gave utilizations around 11%. The BET surface area analyses of copper oxide powder produced by the latter preparation technique have ranged from 4 to

26 m²/g. This may be compared to the surface area of 1 m²/g reported last quarter for the technical grade copper oxide powder.

A quartz reaction tube was installed in the microbalance unit apparatus to permit high temperature operation. This permitted samples to be prepared in a much more controlled manner inside the furnace of the microbalance unit. Small samples of copper sulfate pentahydrate were decomposed to copper oxide powder at peak temperatures of 650°C, 700°C, and 750°C in air or nitrogen. In all tests, the thermal decomposition was followed by absorption in simulated flue gas at 550°C and a second decomposition step at the same conditions as the first. Results showed that utilization of the copper oxide powder was 40% to 60% and that regeneration of the sorbent in the next decomposition step was 80% to 100%. These results do not as yet show any definite trends due to successive refinements of the testing procedures.

In the next quarter, an extensive parametric testing program will be conducted on the microbalance unit using copper oxide powder prepared by decomposing copper sulfate pentahydrate. Other copper oxide preparations will be made and tested on the microbalance. Preparations showing high reactivity will be subjected to parametric testing. Construction of the packed-bed reactor unit will begin at either the original or an alternate site.

Advanced Separation Techniques for Application to SO₂/NO_x Cleanup Processes

*R.J. Walker, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch*

The objective of this project is the evaluation of potential applications for advanced separation techniques in flue gas cleanup processes. Advanced separation methods include the following: membrane separations, supercritical extraction, liquid-liquid extraction, ion exchange, resin adsorption, solvent extraction, and electrophoresis.

A review of existing wet simultaneous SO₂/NO_x cleanup processes has been completed. Work continued to identify steps in 14 existing wet simultaneous SO₂/NO_x absorption processes where advanced separation techniques may be applied. The most promising modifications identified so far are to replace ferrous EDTA with ferrous oxalate in the Mitsui Process and to supplement steam stripping with solvent extraction to

reduce steam requirements; to separate nitrogen and sulfur species, preventing them from interacting; and to produce a useful by-product (sulfur) after reaction of SO₂ and added H₂S. A purchase order was issued to translate a Japanese report describing tests of NO absorption by 100 additives, including ferrous oxalate. Oxalic acid should buffer the solution at pH values of about 1.3 and 4.3. The latter should be satisfactory for SO₂ absorption. An existing computer program was modified to calculate SO₂ vapor pressure over partially neutralized oxalic acid solution. The calculated SO₂ vapor pressures were satisfactory.

A process was identified that could remove both SO₂ and NO by electrodialysis. Previous processes using electrodialysis removed only SO₂. The new process requires bipolar water-splitting and other membranes.

In another process, a spent absorbent is heated to cause it to separate into two phases. It is to be hoped that one of these contains most of the pollutant and can be steam-stripped with reduced steam requirements. An aqueous solution of N-cyclohexyl-2-pyrrolidone appears promising, as it has been found to absorb NO₂ and SO₂ during studies conducted at the University of Pittsburgh under this project. As it is not known if this solution absorbs NO, an additive to absorb or oxidize NO might be necessary. The vapor pressure of N-cyclohexyl-2-pyrrolidone was estimated to be 0.028 torr at 50°C, which could cause excessive stack losses. However, experimental results with similar compounds indicate that excessive stack losses could be prevented by two or three plates of water wash at the top of the flue gas absorption column.

Lurie Process Evaluation

*F.E. Spencer, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch*

The objective of this project is to conduct a laboratory-scale parametric evaluation of the sodium aluminate process invented by Dr. David Lurie. Specifically, this effort is to evaluate the potential for absorption of sulfur dioxide and nitrogen oxides by a series of measurements of vapor pressures over a sodium aluminate slurry as a function of concentration, temperature, and slurry pH.

The site of the counterflow reactor is being changed to accommodate space requirements in the laboratory. Therefore, testing will not begin before August, 1984. Tests will be conducted to

ensure pumpability of the slurry and good operation of the counterflow reactor before measurements can be made.

In order to simulate the sulfur absorption chemistry of the Lurie Process, aqueous sodium aluminate (NaAlO_2) solution is being titrated with 10% sulfuric acid. Beginning at a pH of about 1.0, $\text{Al}(\text{OH})_3$ floc is redissolved as $\text{Al}_2(\text{SO}_4)_3(\text{aq})$. Variations in the titration curve with temperature and NaAlO_2 concentration are being studied. An additional pH breakpoint, expected to occur at low pH after the $\text{Al}(\text{OH})_3$ floc has redissolved, was not observed. Experiments with more concentrated acid are being considered.

Fossil Energy/Resource Conservation and Recovery Act Support

C.M. White, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The overall objective of the Fossil Energy Technology Waste Sampling and Characterization Program is to develop the needed data base to define the hazard potential of such wastes after disposal. The data base is presently incomplete, particularly with respect to potentially hazardous organic constituents. The purpose of the proposed work is to provide analytical information whose validity and precision are established. Development of the data base will aid the Agency in complying with the Resource Conservation and Recovery Act (RCRA) as it relates to solid wastes from fossil energy technologies.

To aid in the achievement of this objective, a multilaboratory effort is being coordinated by the PETC Analytical Chemistry Branch for the development and application of an analytical methodology for the analysis of organic constituents in leachates, thus allowing an evaluation of potentially hazardous constituents.

During the past quarter, an ASTM D-34 Committee meeting on Waste Disposal was held in Arlington, Va. Personnel from PETC attended this meeting and presented an update to the Subcommittee on Organic Analytical Methods. Additionally, results of the Section Level ballot were presented. Plans to conduct a round-robin study of the "Proposed Method for the Determination of Semi-Volatile Organic Compounds in Aqueous Leachates of Wastes" were discussed. Personnel from PETC chaired a meeting of ASTM Task Force D.34.02.04-01 at which the final qualitative analytical results obtained during analysis of an EPA solid waste leachate were presented.

Administrative issues have been resolved so that the quantitation experiments necessary to begin the final ASTM round-robin testing of the proposed method can be completed. Samples for the round-robin should be distributed to the participating laboratories before the end of the fiscal year.

A manuscript entitled "Round-Robin Investigation of Organic Compounds in Aqueous Leachates of Solid Wastes: Application to H-Coal Filter Cake Leachates" was submitted to internal review. Next quarter, the manuscript will be revised to incorporate the reviewers' comments.

UTILIZATION: COMBUSTION TECHNOLOGY

G.T. Bellas, Coordinator

The purpose of this program is to develop the technology for retrofitting oil- and gas-designed industrial boilers to burn alternate fuels, such as coal-water mixtures, and to provide the data base needed to evaluate the technical, economic, and environmental aspects of using alternate fuels in both existing and new applications. Combustion tests with coal-water mixtures (CWM) are being conducted in a 700-hp (24,000 lb of steam per hour) watertube boiler designed to burn fuel oil. Various approaches to burning CWMs efficiently and with minimum NO_x emissions will be evaluated. Combustion tests with alternate fuels are being conducted in a 100-hp (3450 lb of steam

per hour) firetube boiler designed to burn fuel oil. Candidate fuels include coal-alcohol, coke-water, and peat-water mixtures; unique retrofit burners will also be evaluated. A fuel rheology laboratory provides specific information and analysis on the fuels to be used in the 700-hp and 100-hp boiler test programs.

During this quarter, a test program to evaluate and optimize the performance of a recently installed low- NO_x combustion system was initiated in the 700-hp boiler using a commercial CWM containing 70% coal. During CWM shakedown tests, NO_x emissions were reduced to 385 ppm while

operating with 13% excess air preheated to 500°F. The NO_x emissions in previous combustion tests with the same fuel and air preheat before installation of the low-NO_x combustion system averaged 500 ppm at excess air levels ranging from 7% to 20%. An earlier pulverized bituminous coal combustion test in the 700-hp boiler achieved carbon conversion and boiler efficiencies of 98% and 82%, respectively, when operating the boiler at full load at 40% excess air level using combustion air preheated to 500°F. The CWM testing in the 100-hp boiler with the rotary cup burner manufactured by Preferred Utilities Manufacturing Corporation has been concluded. An improved rotary cup burner assembly was designed in-house and is being fabricated for testing next quarter. An ultrasonic burner, manufactured by the Sonic Energy Combustion Systems, was installed in the 100-hp boiler, and shakedown tests with CWM fuel were conducted. Viscosity measurements were performed in the fuel rheology laboratory on slurries prepared with run-of-mine and beneficiated coals in water or in water-methanol in an effort to explain the significant effect of coal cleaning on slurry properties.

700-hp Combustion Test Facility
G.T. Bellas, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch

The objective of this project is to determine the feasibility of using coal-water mixture (CWM) fuels in industrial boilers designed to burn fuel oil. During this quarter, the Coen Company low-NO_x-burner was installed to incorporate staged combustion. The low-NO_x-burner optimization tests with a commercial CWM are being conducted. Prior to the delivery of the low-NO_x-burner design from the Coen Company, an exploratory pulverized coal combustion test was conducted in the oil-designed 700-hp watertube boiler.

The major modifications made on the 700-hp boiler for staged combustion were the installation of three air ports on a side wall of the boiler downstream of the primary combustion zone, an air duct, and flow control and measuring instruments. Base-line tests were conducted initially with the three air ports blocked with refractory plugs. A commercial CWM fuel, ARC-COAL, that was produced by the Atlantic Research Corporation and contained 70% Eastern U.S. bituminous coal was used. The combustion air was preheated to about 500°F, and the atomizing air to fuel ratio and the center-tube air to secondary air ratio were

kept at optimum conditions of 0.4 lb air/lb CWM and 0.34, respectively.

For staged combustion tests, an optimum air port size and configuration that yielded the lowest NO_x emissions and optimum combustion efficiency were initially identified. For a given amount of the combustion air diverted through NO_x ports, the linear velocity of air is affected by the cross-sectional area of the port. The velocities and trajectories of air stream at these ports influence the flame pattern and the effectiveness of the staged combustion. During the shakedown tests, it was determined that the use of three 4.5-inch x 4.5-inch ports with baffles installed in each port appeared to give the optimum flame pattern. The baffles in the center air port were angled 31° from the perpendicular line to the flame envelope towards the rear of the furnace. Baffles in the top and bottom ports were angled 18° from the same line towards the rear of the furnace. With the above configuration, the staged air could be prevented from being drawn into the primary combustion zone by the strongly recirculating flame. Preliminary tests were conducted with approximately 75% to 100% of stoichiometric air passing through the burner with 100% of the fuel while the remaining air needed to complete combustion was diverted through the side-wall NO_x ports. The NO_x emissions were reduced to 385 ppm while operating with 13% excess air preheated to 500°F and with the burner primary zone at a stoichiometric ratio of 76%. The NO_x emissions in previous combustion tests with the same fuel and air preheat prior to installation of the low-NO_x combustion system averaged 500 ppm at excess air levels ranging from 7% to 20%. Formal tests will begin next month to determine optimum low-NO_x operating conditions and to acquire information on carbon burnout.

Before the low-NO_x-burner installation, the 700-hp boiler was operated at full capacity while burning a pulverized Eastern Kentucky coal with a particle size-consist of 94% minus 200 mesh. During testing of three burner configurations, it was determined that a 6-inch burner with a 60° counter-current primary air diffuser positioned at the end of the guide pipe produced the most stable flame. A stable pulverized-coal flame was produced at full boiler load without natural gas support using secondary air preheated to 500°F. Boiler-operating parameters were set to maintain the best flame appearance while maintaining a 5.5% O₂ level in the flue gas. A primary air/secondary air ratio of 0.12 was maintained throughout the test.

Table 20.
700-hp Boiler Combustion Test Using Pulverized Coal and CWM

	<u>Pulverized Coal</u>	<u>CWM</u>
Fuel Composition, %		
Dry Coal	98.7	62.5
Water	1.3	37.5*
Heating Value, Btu/lb	14,612	9,224
Ash in Coal, %	2.5	3.3
Coal Size-Consist (% minus 200 mesh)	94	90
Combustion Air Temperature, °F	532	493
Excess Air, %	41	14
Steam Flow, lb/hr	24,000	24,100
Carbon Conversion, %	98.3	96.5
Boiler Efficiency, %	82.3	78.1
Heat Loss Due to Water in Fuel, %	0.1	4.6

*Includes 0.5% Lomar-D, a surfactant.

The results are shown in Table 20 and are compared with those obtained from combustion tests using a CWM prepared with a similar Eastern Kentucky coal. The carbon conversion and boiler efficiencies were 98.3% and 82.3%, respectively, when operating at a 41% excess air level. In comparison, the test with the CWM achieved carbon conversion and boiler efficiencies of 96.5% and 78.1%, respectively, when operating at a 14% excess air level. The difference in the boiler efficiency between the two fuels was mainly due to the heat lost in evaporating the water in the CWM.

100-hp Combustion Test Facility
G.T. Bellas, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch

The objective of this project is to examine the potential of alternate fuel mixtures to replace fuel oil firing in conventional combustion equipment. The project includes an identification of promising combinations of fuel mixtures, the actual combustion testing of the identified mixtures in PETC's 100-hp Alternate Fuel Mixture Combustion Test Facility, and technical, economic, and environmental assessments and recommendations.

During this quarter, testing with the rotary cup burner manufactured by Preferred Utilities Manufacturing Corporation was concluded. An improved rotary cup burner assembly was design-

ed in-house and is being fabricated for testing next quarter. An ultrasonic burner, manufactured by the Sonic Energy Combustion Systems, was installed in the 100-hp boiler. Shakedown testing with the ultrasonic burner was also conducted.

During the last quarter, the rotary cup burner provided by Preferred Utilities was tested with a coal-water mixture (CWM) in its originally designed configuration for firing No. 6 fuel oil. This configuration was characterized by the injection of secondary air into the boiler at positions much removed from the point of CWM injection. A change was made to redirect the secondary air through a 1-inch-wide annular space surrounding the nozzle. A moderate amount of swirl was imparted to the secondary air by a diffuser installed within the secondary air stream. Four different angled (7½°, 15°, 22½°, and 30°) rotary cups were evaluated in conjunction with two primary air swirlers containing vane angles of 30° and 45°. Although the flame appearance improved, an independent CWM flame still could not be established without natural gas support. An in-house designed rotary cup burner assembly that would be adaptable to the previously used 22-inch swirl vane air register has been fabricated. Testing will begin in the next quarter.

The 100-hp boiler was also modified to accommodate the Sonic Energy Combustion Systems ultrasonic burner for CWM combustion. Its atomizing nozzle uses compressed air to create

an intense sonic shockwave. As the pressurized air expands through a converging-diverging section and into a resonator cap at supersonic velocity, the reflected shock waves focus the sonic energy between the resonator cap and the body of the nozzle. As CWM is pumped into the shock wave, fine droplets are formed and sprayed into the combustion chamber. The ultrasonic burner is expected to improve the burner performance by increasing combustion efficiency and reducing fuel consumption.

Shakedown tests were conducted with a commercial CWM containing 70% bituminous coal using combustion air preheated to 500°F. Different ultrasonic burner configurations (i.e., different sized nozzles, washers, and resonators) were tested, but the main obstacle was plugging within the nozzle when CWM was fired. Switching of the atomizing air and fuel paths in the burner, however, led to the establishment of a stable CWM flame. Under these conditions, the fuel mixture was introduced through the center path of the nozzle and was sheared by compressed air exiting small orifices around the burner perimeter. The improvement was in effect owing to the external mixing atomization rather than the sonic atomization. Technical representatives of the Sonic Energy Combustion Systems are planning to redesign their ultrasonic burner, probably incorporating the sonic atomization effect in the external ports. Further testing will be carried out when a modified ultrasonic burner is completed.

Fuel Rheology Laboratory

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Combustion Technology Branch

The laboratory has completed the slurry projects that were planned for Dr. M. Chakraborty. Dr. Chakraborty, a visiting Indian scientist, was able to obtain the information he desired about laboratory instruments and about the properties of slurries prepared from various Indian coals. Laboratory technicians, at his request, planned and carried out his experiments and demonstrated the operation of the laboratory equipment; Dr. Chakraborty plans to establish a similar rheology laboratory upon his return to India and to continue research with Indian coals.

Viscosity measurements are being made on slurries prepared with run-of-mine and beneficiated coals in water or in water-methanol; tests are underway with Pittsburgh and Lower Kittanning coals, and other coal types are on hand. Although these tests are still in the early stages, some

viscosity measurements on Kittanning coal-water-methanol slurries have been graphed as a function of percent methanol (see Figures 13 and 14) and there appear to be differences in the

Figure 13. Viscosity vs. percent methanol in water-methanol and in 60 % Lower Kittanning-2 coal-water-methanol slurries

Figure 14. Viscosity vs. percent methanol in water-methanol and in 58 % Beneficiated Lower Kittanning-2 coal-water-methanol slurries

shapes of these curves, as well as in the magnitudes. The reasons for these differences are not obvious from the initial tests. Chemical analyses, and measurements of density and of surface area showed no significant differences other than the expected ash reduction. It is expected that continued analyses of slurry viscosities and of other physical and chemical properties will demonstrate patterns and perhaps suggest some explanations for the effects of coal cleaning on slurry properties.

To evaluate new test procedures, dynamic and static stability were measured during several one-week tests on CWMs with varying makeups. Results indicated that the tests are not sufficiently sensitive: no significant changes were detected under any of the conditions tested. The stability tests must be redesigned or at least extended in duration. A Brookfield viscometer capable of recording changes in viscosity in a sample sheared for an extended period has been obtained from surplus; however, this instrument must be repaired before it can be used as a part of stability testing.

New tests are planned to evaluate CWM viscosities at high rates of shear, and the extrusion rheometer is being rebuilt to carry these tests out. Although previous tests using this capillary style viscometer were unsuccessful, it is anticipated that new procedures can be developed that will allow routine high-shear measurements for stable slurries.

A series of viscosity measurements was made on a liquid viscosity standard and on a coal-water-methanol slurry to demonstrate the degree of scatter that seems to be unavoidable in slurry measurements. Repeated measurements with the Newtonian standard were virtually identical; repeated measurements of the slurry fluctuated widely and followed no discernible pattern over time. Each measurement was made on a fresh aliquot from a large, stirred sample, and sampling conditions were as consistent as was possible. Measurements of apparent viscosity varied by hundreds of centipoise under identical conditions, and the tendency to thicken or thin with time also seemed to vary. The actual degree of scatter has been observed to change with slurry makeup, and significant fluctuation appears to be unavoidable. A series of viscosity measurements is indicated in situations in which precise viscometric information is desired.

Slurries, containing mixtures of acrylic spheres, which will be used to model coal slurries, have been prepared and observed. A small percentage of fluorescent spheres was mixed with the ordinary spheres evaluated previously. Visual observations of particle movements were very clear when a beaker of this mixture was agitated under ultraviolet light, and a videotape was successful. It is planned to duplicate this fluorescent mixture in the CWM flow loop and to observe and film flow behavior as the spheres move through a glass elbow that will be installed in the loop.

DIRECT LIQUEFACTION

G.J. Stiegel, Coordinator

This program is concerned with engineering studies related to various aspects of direct coal liquefaction. Experimental investigations are directed at understanding the chemical and physical processes occurring during the liquefaction of coal with supercritical water, the evaluation of the activity and deactivation characteristics of supported-metal catalysts for the hydroprocessing of coal liquids, and the development of a technique for fractionating nondistillate coal liquids. Process modeling using commercially available process simulators is being conducted to evaluate the consistency and completeness of the existing coal liquefaction data base.

A series of experiments using the fractional distillation vessel was initiated to determine the effect of reflux, using the hot-finger zone, on the

degree of residuum fractionation. The difference in residuum concentration between operations with and without reflux shows that a large part of the residuum being transported from the pot is rejected due to the higher temperatures, thus lower fluid density, in the hot-finger zone.

In place of experimental yield distributions for the ASPEN modeling of Gulf's P-99 coal liquefaction unit, Gulf's kinetic reaction model was inserted as the reactor module for the simulations. This model assumes an instantaneous dissolution of coal to SRC-type product, followed by conversion of the SRC to a fixed ratio of products. Preliminary results using the kinetic model indicate that shifts in the product, yields compared to previous results using experimental yield dis-

tributions have little impact on the internal stream flow rates.

An existing one-liter stirred autoclave reactor system was modified for conducting coal liquefaction experiments using supercritical water. The unit is approximately twenty times larger than the microautoclave reactors currently being used and will produce sufficient product for detailed characterization. Several preliminary tests using Illinois No. 6 River King coal were conducted over a temperature range of 700°F to 892°F and pressure range of 4000 psig to 4500 psig.

American Cyanamid recently reported that their microfiltration test used to determine conversions of coal or resid based on solubility in selected solvents was dependent on the amount of solvent used to wash the sample. The validity of this result was checked by washing two different-size samples with different amount of solvent. No effect of washing was found, but small differences were observed between sample sizes due to dilution effects. These results confirm the arbitrary nature of solvent analyses and suggest the need for a standardized procedure for interlaboratory comparisons.

In the investigation of the thermal component of residuum conversion, four solvents having different concentrations of hydrogen were reacted thermally at 720°F and 750°F in the continuous hydrotreater. Analyses of the feed and products by mass spectroscopy showed very little hydrogen rearrangement. Approximately 10 wt% of the 850°F+ material was converted thermally, but almost no material was converted to 650°F- product. Very little reduction in heteroatom concentration occurred. These results indicate that the conversion of residuum in the hydrotreater is catalytic rather than thermal.

Liquefaction Bottoms Fractionation

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J.A. Ruether, Chief,

Coal Conversion Engineering Branch

The objective of this project is to develop and apply improved methods for describing the behavior of liquefaction bottoms in vapor/liquid separations under conditions of vapor/liquid equilibrium (VLE) that exist in liquefaction processes. Initially the project aims to develop a method of fractionating liquefaction bottoms into a number of cuts, or pseudocomponents, that are more amenable to characterization than whole bottoms. The VLE data for the pseudocomponents will be determined directly by experiment

and indirectly from compositional data. The pseudocomponent VLE data will be combined to establish correlations describing the unfractionated bottoms.

During this quarter, the accuracy of pressure measurement in the Fractional Destruction Vessel (FDV) was improved by the incorporation of an additional pressure sensor located on the supercritical fluid inlet line to the FDV. During the previous quarter, the accuracy of the pressure measurement device located at the outlet of the column was found to be sensitive to the temperature of the process stream. This sensor is required in this hot zone for control of a nearby research control valve. The new sensor, however, is maintained at near ambient temperature by isolating it from the hot fluid by a length of stainless steel tubing. The new sensor is calibrated against both a digital and mechanical Heiss gauge before each experiment, thus providing the accuracy needed to continue investigation of the primary process variables. A correction factor was determined by comparison of the readouts of these two sensors while heating the original sensor. The observed deviation was as high as 90 psi at a temperature of 340°C, measured below the inlet to the original sensor. This will allow correction of pressure data from previous experiments.

After the above-mentioned modifications were made, an experiment was repeated in which a charge of residuum from the T102 separator at Wilsonville was subjected to incremental increases in operating pressure using cyclohexane as the supercritical fluid. The original experiment was reported in the last quarterly report. The FDV was at isothermal conditions (hot finger off) so that base-line destruction data were obtained. Figure 15 depicts the results of the recent experiment. The pressure increments were approximately 30 psi. Note the sharp increase in residuum carry-over at a density near 0.2 g/cm³. This was also observed in the previous experiment; however, the pressure values are now more accurate. The older data agree with the current results if the pressure correction discussed above is used. At this temperature (291 ± 2°C), it would not be possible to further subdivide the 30-psi range to produce fractions by incremental pressure changes, since the practical limit of pressure control in this region is ± 4 psi. Based upon these results, we decided to operate at P_R of 1.25 in the next series of experiments in which the hot finger would be used.

A series of experiments was initiated this quarter in which the temperatures of the hot finger

Figure 15- Destruction of TiO₂ bottoms with cyclohexane at $T_R = 1.02$

and packed bed were varied to determine the effect of promoting reflux on the degree of fractionation. The temperature of the FDV pot was maintained at a T_R of 1.02 and a P_R of 1.25 as discussed above. Figure 16 compares the results from two of these experiments, one in the reflux mode using only the hot-finger zone to promote reflux and another at isothermal (no reflux) conditions for comparison. The difference in the

overhead concentration of residuum shows that a large part of the residuum being transported from the pot is rejected due to the higher temperatures, and correspondingly lower densities, in the hot-finger zone. Some of the initial characterization of the fractions from both of these experiments is discussed in the companion quarterly report entitled "Bottoms Characterization."

Plans for the next quarter include completion of the current series of experiments concerning fractionation under reflux conditions. A series of identical experiments will then be performed using the best set of operating parameters determined to date to yield the sharpest fractions from the Wilsonville residuum. If successful, the corresponding fractions obtained from each experiment will be combined to provide a larger quantity of individual fractions for more extensive testing, including VLE measurements in an ebulliometric still.

ASPEN Modeling

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J.A. Ruether, Chief,

Coal Conversion Engineering Branch

The purpose of this program is to establish a direct liquefaction process modeling capability of general utility in future years. The process simulator of choice is ASPEN (Advanced System for Process Engineering). Process modeling pro-

Figure 16- The effect of using a temperature gradient to promote reflux

vides the opportunity and method to verify the consistency and completeness of existing data bases in coal liquefaction. It can also complement DOE-sponsored experimental development of third-generation liquefaction processes by computing material and energy balances for test cases and by providing estimates of the economic consequences of process design changes. Process modeling capability will be developed using the existing SRC-II data base from Gulf's P-99 Process Development Unit. Results from the unit are judged to be the most complete and accessible of any unit under consideration.

During this quarter, ASPEN simulations were completed for nine liquefaction tests that had been conducted in Gulf's P-99. Liquefaction variables investigated in the experimental data sets were coal source, reactor dimensions, temperature, hydrogen partial pressure, and solids concentration. The experimental data included flow rates and compositions of internal streams into and out of key process vessels. The ASPEN-calculated values of component flow rates can thus be compared readily to the data sets, and the success of the simulations can be evaluated.

Each P-99 run was simulated three ways, for a total of 27 simulations. Two different assumptions for describing the behavior of nondistillate organic material (SRC) in separation vessels were tested. Accurate prediction of vapor/liquid splits in vessels handling SRC-containing materials, such as in the hot high-pressure separator, is especially important in order to mitigate error propagation throughout the rest of the integrated flow sheet. An assumption of a linearly decreasing boiling point distribution for the SRC in conjunction with the Redlich-Kwong-Soave equation of state gave a mean error of less than 20% in the vapor flow rate out of the hot separator, compared to published errors on the order of 30%. The mean error decreased to less than 10% with an empirically assigned single nominal boiling point of 1400°C for the entire SRC fraction.

In the third set of ASPEN simulations of the P-99 unit, Gulf's kinetic reaction model was inserted as a reactor module in place of the experimental yield distribution used before. The boiling point of the SRC was assumed to be 1400°C. The reaction model describes coal conversion to occur in two steps: an instantaneous dissolution to mostly SRC, followed by conversion of the SRC to a fixed ratio of products in a rate-controlled, second step governed by temperature, hydrogen partial pressure, and mass frac-

tion of ash in the reactor. Preliminary analysis of the ASPEN outputs suggests that shifts in the product yields calculated via the kinetic model have only a weak impact on the internal stream flow rates. The mean error in the vapor flow rate out of the hot high-pressure separator, for instance, was again less than 10%.

Next quarter, a detailed comparison will be drawn between the nine P-99 experimental data sets and the ASPEN process simulations of the same tests.

Supercritical Liquefaction

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Coal Conversion Engineering Branch

The objective of this project is to conduct engineering research directed toward effectively transporting coal slurries through a preheater and understanding the phenomena governing fluid/solid transport and heat transfer as related to conventional and novel coal liquefaction techniques. Another objective is to identify optimal reaction conditions for the preheater and reactor. A third objective is to continue the development of a capillary tube viscometer for use in measuring coal-slurry viscosities at process conditions. The objectives are interactive. Optimal reaction conditions must be found within the boundary of operating conditions that permit movement of feed slurry into the reactor while heating it to the required reaction temperature.

During this quarter, work was performed in the following areas:

A. Design and Operation of a Bench-Scale Preheater for Coal/Water Slurries

In an attempt to discover alternative processing techniques that will reduce the capital costs for direct coal liquefaction, the use of supercritical water to convert coal to liquid products presents many attractive advantages. When compared to conventional donor solvent liquefaction processes, the use of an organic liquid vehicle is eliminated, and potentially a greater fraction of the reactor volume would be available for coal if a concentrated (65 wt% to 70 wt% coal) coal/water slurry is used. As well, it may be possible to operate without a separate heavy liquid/solids removal step if the dissolving power of the supercritical fluid mixture in the reactor is sufficiently great. In addition, the feed coal could be impregnated with a catalyst that may subsequently be recovered from the solid residue for reuse.

A continuous-processing approach currently being considered employs a concentrated coal/water slurry that is passed with a reducing gas through a preheater and into a backmixed reactor. The high-temperature portion of the preheater would operate in the supercritical region with respect to the water and reducing-gas mixture. Vapor and liquid products would be removed from the reactor in the fluid phase at the top of the reactor, while solids will be removed at the bottom.

In considering the possible experimental difficulties that may be encountered in designing and operating such a preheater, one of the greatest concerns is in determining the transport characteristics of the slurry as it approaches the critical point. For this reason, a bench-scale preheater in which coal/water slurry can be pumped and heated to supercritical conditions will be designed, constructed, and operated. Transport data collected from tests performed in this apparatus will be correlated with fluid flow models.

From a literature review of fluid/solid transport with application to a process for aqueous coal liquefaction, recommendations were developed for designing a bench-scale preheater for the particular case of heating a concentrated slurry of coal and water at a pressure of 4000 psig over a temperature range of 100°F to 800°F. A schematic diagram of the proposed preheater system is shown in Figure 17. Coal/water slurry from a steam-jacketed, stirred feed tank is pumped at a pressure of 4000 psig through the preheater and cooler to a high-pressure product-holding tank that is periodically drained.

From a simplified single-phase flow model, the momentum and heat transfer characteristics of the coal/water slurry preheater operating at nominal linear velocities of 1, 3, and 5 ft/sec at the preheater entrance were calculated. The resulting fluid temperature and pressure drop curves are shown in Figure 18 for the specific test conditions: 4000 psig pressure; 0.500-in.-o.d. x 0.083-in.-wall tube; and a constant outside tube wall temperature of 1000°F. The model further assumes that the coal/water slurry is a homogeneous, Newtonian liquid with a viscosity of 160 cp, since the physical properties of coal/water slurries are not available at conditions of elevated temperature and pressure. As noted in the figure, the heat-up to 800°F can be achieved in all instances; however, the apparent pressure drops become excessive at the higher linear velocities. A more complex, two-phase flow model for the preheater is currently being developed to determine the effects of adding hydrogen gas to the preheater as an auxiliary transport medium. These calculations will also be verified by commercially available process simulators (Pipeflo® and Pipephase®).

Construction of the coal/water slurry preheater is in progress. The preheater consists of 221-ft of 0.500-in.-o.d. x 0.083-in.-wall, 316 stainless steel tubing that is coiled and immersed in a fluidized-sand-bath heater that can be maintained at temperatures up to 1000°F. Following fabrication and pressure testing with both high-pressure hydrogen gas and water, the preheater coil was mounted in the fluidized-sand-bath heater. Shakedown testing of the heating, control, and fluidizing-gas-delivery systems has begun.

Figure 17- Coal/water slurry preheater apparatus

Figure 18 - Fluid temperature and pressure drop versus tube length for a coal/water slurry preheater

Two different plunger pumps have been ordered for use as the high pressure feed pump. While both pumps are capable of pumping up to 50 gal/hr of concentrated coal/water slurry to discharge pressures in excess of 5500 psig, one pump is being supplied with a tungsten carbide coated plunger and check valves, and the other

with ceramic internals. A performance evaluation of each pump will determine the more abrasion-resistant material for future applications of this concept.

The remaining major equipment components (slurry feed tank, slurry recirculation pump, fluidized-sand-bath heater, and product-holding tank — 5-gal stirred autoclave) with the exception of the cooler are available at PETC. Potential means of cooling the hot slurry are currently being evaluated.

B. Batch Autoclave Studies

Prior to beginning a continuous processing scheme, a number of scoping studies are being performed by the Process Sciences Branch in a microautoclave apparatus employing a fluidized-sand-bath heater. These experiments will justify the process concept and determine the optimum conditions for operation.

An existing 1-L stirred autoclave apparatus was modified to conduct experiments in which the results obtained in the microautoclave studies can be verified in a larger apparatus. Capable of operating at temperatures up to 850°F and pressures up to 5000 psig, the effective volume and charge weights of the stirred autoclave apparatus are approximately 20 times that of the microautoclave. Therefore, in addition to verifying the microautoclave results, the liquid and solid products will be produced in sufficient quantity to permit detailed characterizations and further testing. As opposed to the microautoclave tests in which the test pressure is estimated, the stirred autoclave system allows measurement of pressure. A back-pressure regulator controls pressure, relieving excess pressure during heat-up periods. Gas vented during the heat-up is collected in a water-sealed gas holder, metered, and sampled. Product gas, after the reactor has been cooled, is collected in the same manner. A water-cooled condenser on the gas exit line from the reactor refluxes water and low-boiling products back to the reactor. Approximately 2 hours are needed to heat the reactor to test temperatures. Post-test cooling is at about the same rate.

Water and oils having a normal boiling range of 530°F to 550°F are removed from the reactor by vacuum stripping at 230°F and 1-mm to 2-mm mercury pressure. Residue in the reactor is removed with toluene, which is then stripped off. The dry residue is analyzed for ash and solubility in tetrahydrofuran to determine the amount of coal charge converted.

Experiments to date have been made at temperatures of 700°F, 800°F, and 842°F, and pressures of 4000 psig and 4500 psig. The basic charge consists of coal, a coal-derived solvent, water, and catalyst. The coal is a bituminous Illinois No. 6 from the River King mine. Ammonium paramolybdate in concentrations of 0.50 wt% and 0.25 wt%, based on coal, is the catalyst.

C. Viscometer Development

In a project to measure transport coefficients in a coal liquefaction preheater, a capillary tube viscometer was developed to determine viscosities of coal-derived liquids on-line in liquefaction processes. This device was recently tested on several Newtonian liquids at conditions of elevated temperature (500°F) and pressure (2000 psig), with an error not exceeding 5%. For this study, a 2.5-L stirred autoclave serves as the pressure/reaction vessel. Fluid is sampled (300-cm³ maximum volume) by opening a valve that couples the autoclave to a precisely controlled metering pump and withdrawing the pump's 2-in.-diameter piston with a computer-controlled motor. A forward pressure regulator reestablishes the pressure equilibrium. The inlet valve is closed and the outlet valve coupling the capillary tube (0.148-in.-i.d. x 19.25-ft-long) with the autoclave is opened. The compumotor piston is moved forward at three or more precisely controlled velocities, returning the fluid sample to the autoclave through the capillary. Stream pressures at the inlet and outlet of the capillary are transmitted to a differential-pressure transducer by lines filled with the test fluid. Flow rate and pressure drop data are fed to a data acquisition computer and evaluated automatically such that a complete flow curve can be generated with a single sample. "On-line Capillary Tube Viscometer for a Continuous Liquefaction Unit," a complete apparatus description and up-to-date summary of the data analysis and results, was presented at the AIChE 1984 Spring National Meeting, May 20-23, 1984, Anaheim, Calif.

The viscometer pump is currently being modified for use in measuring the viscosity of coal slurries at elevated temperature and pressure. Each of several attempts to measure the viscosity of commercially prepared coal-water mixtures has failed. A detailed analysis of each failure has indicated that the annular space between the pump's piston and cylinder (0.007-in.) is large enough to trap the finely pulverized coal particles and restrict the movement of the piston by increasing friction. A set of specially sized piston

rings is currently being manufactured to prevent the migration of coal particles between the piston and cylinder wall.

Catalyst Preparation and Characterization

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Coal Conversion Engineering Branch

The objective of this project is to enhance the development of direct coal liquefaction processes by providing fundamental data on the hydrotreating of coal liquids by supported-metal catalysts. Two approaches are involved in attaining this objective. The first is the evaluation of the factors involved in the preparation of new catalyst compositions and determining their effect on catalytic activity. The effect of support on carbon deposition is the main focus of this approach, with the effect of the promoter/active metal ratio being explored in less detail. The second approach involves characterization of spent coal-liquefaction catalysts to determine the type of metals deposition and coke buildup occurring during aging and how it is affected by changes in processing conditions.

This cost account and related personnel were transferred from the Process Sciences Branch to the Coal Conversion Engineering Branch. Equipment for catalyst preparation and product work-up was moved to a new location. The move to the new laboratory was completed this quarter, and all the equipment is operational. The batch autoclave test was suspended this quarter while effort was directed towards setting up more realistic product-characterization tests. Currently, the catalyst is evaluated for hydrogenation and heteroatom removal activity as determined by elemental analysis and conversion of SRC. Since the quality of a recycle solvent is not directly related to any simple property of the solvent, it was decided to set up additional tests.

A distillation unit was set up to obtain the 650°F+ fraction from the autoclave products and to determine the activity of the catalyst to convert SRC to material boiling below 650°F. The fraction boiling above 650°F will be tested for solvent quality using an empirical tubing-bomb test, such as that used at Wilsonville and Conoco. During the coming quarter, the products from the Ni-Mo/Al₂O₃ catalyst runs will be distilled to determine 650°F+ conversions and to obtain material that will be used for the tubing-bomb tests. Autoclave testing of the Ni-W/Al₂O₃ catalysts will re-

sume, and conditions for the tubing-bomb solvent-quality test determined.

Recently, American Cyanamid questioned the procedure used for the microfiltration test. Terry Muchnick of American Cyanamid indicated that they found their microfiltration results to be very dependent on the amount of solvent used to wash the precipitate. Also, she used a much smaller sample size (1 g) than that used at Amoco or PETC (6 g). The validity of her observations was checked using one- and six-gram samples and varying the amount of wash solvent from 400 to 1000 mL. Our results (Table 21) show that there is no washing effect for the six- and one-gram samples. However, the relative amount of insolubles was higher for the tests using a six-gram sample than for those using a one-gram sample, as expected, due to dilution effects. Both the one- and six-gram samples were dissolved in 75 grams of cyclohexane prior to pressure filtration and washing. Indeed, the sample size effect does reconfirm the arbitrary nature of solvent analysis results and points out the need to standardize such tests if results are to be compared between laboratories.

Work is continuing on the effort to prepare metal-free SRC/recycle solvent feedstock, if possible, to decouple the metal and coke effects on catalyst deactivation. Preliminary results indicate that the metals are contained in the preasphal-

of the SRC with ethyl acetate, or precipitated from tene fraction, which was separated by extraction a tetrahydrofuran solution of SRC by dissolving in an excess of ethyl acetate. However, since both methods would cause particulate impurities to concentrate in the preasphaltene fraction, we cannot prove whether the metal is present as particulates or is forming complexes with the preasphaltenes fraction. Quantitative amounts of metals in each fraction have not been obtained yet, owing to lack of reliable standards for the X-ray fluorescence analysis. However, preliminary results indicate that the iron and titanium are not removed by passing a tetrahydrofuran solution of SRC through filter papers ranging from 0.2 to 10 μm . This treatment does remove calcium, which must be present as particulate matter.

Since the metals do concentrate in the preasphaltene fraction, a large amount of this fraction was prepared for subsequent demetalization studies. During this preparation, it was discovered that during extraction of Wilsonville SRC in a Soxhlet extractor open to the atmosphere, a layer of solid was formed on the outside of the thimble during extraction in both ethyl acetate and cyclohexane. Analysis of this material revealed it contains a higher heteroatom content than the original SRC, particularly oxygen. Exposing the SRC to air at 100°C for 16 hours before extraction eliminated the formation

Table 21.
Microfiltration Results for Cyclohexane Conversion*

Sample wt (g)	Filter Pore Size (μm)	Wash Solvent (mL)	wt % insols
1	10	400	14.2
1	10	700	14.1
1	10	1000	13.6
6	10	400	17.2
6	10	700	17.0
6	10	1000	15.8
6	5	400	16.8
6	5	700	16.7
6	5	1000	16.7

*Product for Run LCR-44 (MBP #3). Sample was dispersed by sonication in 75 mL of cyclohexane prior to pressure filtration and subsequent washings.

Figure 19-

of this deposit. This indicates that the Wilsonville SRC contains a very reactive component, which reacts on exposure to oxygen even at 70°C to 80°C.

The solvent precipitation technique would appear to be a good technique for determining if the metals are associated with the preasphaltenes or present as particulates. This technique allows one to selectively precipitate increasing amounts of preasphaltenes (Figure 19). If the metals are present as particulates, they should act as nuclei for precipitating preasphaltenes. As a result, the metals remaining in the SRC should drop off rapidly as increasing amounts of preasphaltenes are precipitated. However, if the metals are chelated by the preasphaltenes, one might expect a linear decrease in metal content as the preasphaltenes are removed.

This coming quarter, the autoclave screening test will be resumed. The activity of the prepared Ni-W/Al₂O₃ catalysts will be tested. In addition, several novel catalysts will be prepared and tested.

Fundamental Studies in Coal Conversion Catalysis

G.J. Stiegel, Cost Account Manager
J.A. Ruether, Chief,
Coal Conversion Engineering Branch

The objective of the proposed research is to provide fundamental data on the hydroprocessing of coal liquids for integrated two-stage coal liquefaction. The program focuses on the evaluation of the effects of catalyst properties on catalyst activity, the phenomena of catalyst deactivation, and the use of new catalyst compositions for the hydrotreating reactor. The effect of the hydrogen content of the SRC solvent fraction of the hydrotreater feedstock on the thermal conversion of the SRC will be assessed. The information obtained will be used to develop a thorough understanding of the chemical and physical processes that affect the performance of the hydrotreater in two-stage coal liquefaction processes, which will provide direction for further investigations leading to process improvements.

Most of the work this quarter was devoted to the evaluation of the thermal component involved in the conversion of residuum. Four solvents were used in the present investigation; their properties are presented in Table 22. Solvent A was obtained from the Wilsonville pilot plant and is the same material that is mixed with the deashed SRC and fed to the hydrotreater. Solvents B, C, and D were produced by hydrotreating Solvent A in a continuous unit at various conditions to achieve different concentrations of hydrogen. Approximate reaction conditions used to obtain these solvents

are presented in Table 23. Sulfiding procedures were almost identical for Solvents C and D. Solvent B was produced using the same catalyst used to produce Solvent C; therefore, the catalyst did not require the full time normally allotted for sulfiding fresh catalyst.

Table 22 also presents the analysis of the residuum that was used in this investigation. For the experimental runs, the solvent was mixed with an equal amount of residuum prior to each run. The feedstock was fed continuously to a con-

Table 22.
Analysis of Feedstocks

	Solvents				
	Residuum	A	B	C	D
Elemental Analysis					
Carbon wt%	88.7	88.6	88.3	88.6	88.9
Hydrogen, wt%	6.76	9.4	9.8	10.5	10.8
Nitrogen, wt%	1.30	0.48	0.28	0.15	0.10
Sulfur, wt%	0.57	0.24	0.06	0.09	<0.05
Oxygen, wt% (by diff.)	2.67	1.30	1.56	0.66	0.20
Hydrogen-to-Carbon Ratio	0.91	1.26	1.32	1.41	1.45
Moisture, wt%	0.05	<0.03	<0.03	1.0	0.4
Ash, wt%	0.2	0.01	<0.01	<0.01	<0.01
Specific Gravity, g/cm ³	1.19	1.026	—	—	0.971
Kinematic Viscosity @ 140°F, cs	—	22.3	16.0	10.5	10.3
Solvent Analysis					
Preasphaltenes, wt%	10.6	0.6	2.3	0.6	<0.2
Asphaltenes, wt%	49.8	4.9	1.4	<0.2	<0.2
Oils, wt%	39.6	9.45	96.4	99.3	99.8
Insolubles by Filtration					
Ethyl Acetate, wt%	—	<0.01	<0.1	<0.01	<0.1
Cyclohexane, wt%	—	1.3	<0.1	<0.01	<0.1
Molecular Weight	577	272	269	255	266
Hydrogen Distribution, %					
H*ar+φ	33	20	17	12	9
H*α	33	27	24	22	20
H*β	28	41	45	50	52
H*γ	6	12	14	16	19

Table 23.
Reaction Conditions for Solvent Preparation

	Solvent		
	B	C	D
Reactor Temperature, °F	720	700	720
Reactor Pressure, psig	2000	2000	2700
Catalyst	Shell 324 (Ni-Mo/Al ₂ O ₃)	Shell 324 (Ni-Mo/Al ₂ O ₃)	RET-60298 (Ni-W/Al ₂ O ₃)
Catalyst Charge, cm ³	80	80	80
Hydrogen Feed Rate, scfh	8	8	8
Solvent Feed Rate, g/hr	180	100	90
Agitation Speed, rpm	1600	1600	1600

Table 24.
Thermal Conversion Results

Solvent	A		B		C		D	
Hydrogen Concentration, wt%	9.4		9.8		10.5		10.8	
Reactor Temperature, °F	720	720	750	720	750	720	750	
ΔH/C, %	-0.5	0.4	-1.0	1.3	0.0	0.8	-0.2	
Denitrogenation, wt%	4.7	10.3	0.0	12.7	0.0	1.5	0.0	
Desulfurization, wt%	0.0	12.5	10.3	9.4	25.9	0.0	12.1	
Deoxygenation, wt% (by diff.)	0.0	0.4	13.3	21.1	12.5	11.5	22.2	
Cyclohexane-Insoluble Conversion, wt%	16.1	0.7	13.1	16.5	14.4	2.1	4.0	
Pentane-Insoluble Conversion, wt%	6.17	5.7	8.5	8.0	7.6	—	8.7	
Molecular Weight Reduction, %	-1.7	4.6	6.5	3.3	4.2	8.3	-1.8	

tinuous stirred tank reactor operating at the following conditions: temperature = 720°F or 750°F; pressure = 2000 psig; slurry feed rate = 109 g/hr (space time = 3.3 hr); gas feed rate = 8 scfh. The products obtained using the four solvents at the two reaction temperatures were subjected to numerous analyses. Table 24 presents a summary of various conversions based upon data obtained by Huffman Laboratory from the ana-

lysis of full-range samples. Similar analyses were also performed at PETC with comparable results. As shown, almost no conversion of the feedstock occurs thermally. Table 25 presents a summary of the results of the distillations of the various feed and product samples. In almost all runs, about 10% of the 850°F + material is converted thermally, which corresponds somewhat to the insoluble conversions shown in Table 24. Very little

Table 25.
Summary of Feed and Product Distillations

Solvent (H ₂ Conc.)	Reactor Temperature, °F	Sample	Distillation			
			<650°F	650°-850°F	>850°F	Loss
A (9.4%)	720	Feed	6.3	27.7	63.1	2.9
		Product	6.6	32.1	58.6	2.7
B (9.8%)	720	Feed	6.4	29.8	62.1	2.6
		Product	7.7	35.2	54.5	2.7
	750	Feed	5.7	27.8	63.9	2.5
		Product	10.1	31.0	55.9	3.0
C (10.5%)	720	Feed	8.6	28.7	59.7	3.0
		Product	10.5	35.9	51.7	1.9
	750	Feed	8.4	28.4	59.8	3.4
		Product	12.2	32.6	52.7	2.6
D (10.8%)	720	Feed	8.2	29.8	59.6	2.4
		Product	8.0	36.6	52.8	2.6
	750	Feed	8.2	29.7	60.7	1.1
		Product	10.4	34.9	51.9	2.8

material, however, is converted to 650°F- product. Further mass spectroscopic analyses of the fractions also confirm the above observations that very little conversion is occurring thermally at the reaction conditions specified. These results indicate that the conversion of the 850°F + fraction of the feed in the hydrotreater is catalytic rather than thermal. Two additional runs have been made with a solvent containing approximately 10.6 wt% hydrogen at 800°F and 850°F to evaluate the extent of thermal reactions on the conversion of 850°F + material under first-stage reaction conditions.

The final series of experiments concerning the effect of catalyst pore size distribution on the conversion of the solvent-refined coal has been started. A series of five catalysts having average pore diameters ranging from 40 Å to 270 Å will be prepared and evaluated in the continuous unit. This set of experiments will employ solvent and

residuum produced at the Wilsonville pilot plant. Reaction conditions for these runs will be as follows: temperature = 735°F; pressure = 2000 psig; VHSV = 0.6 cm³ resid/hr/cm³ catalyst; hydrogen feed rate = 8 scfh. Thus far, two catalysts have been evaluated.

Construction of the batch microreactor system was completed and shakedown is in progress. A product work-up and catalyst preparation area consisting of laboratory benches and fume hoods was installed. Construction of the gas delivery system for the continuous-flow reactor systems has been completed, and work has begun on the installation of the hot-oil-heating system and the continuous-process units. Bids were received for the process control and data acquisition system, and the contract was awarded to Great Lake Controls for a system manufactured by Texas Instruments. The system is scheduled for delivery during the next quarter.

INDIRECT LIQUEFACTION

R.R. Schehl, Coordinator

This program is directed toward developing a better fundamental understanding of catalyst properties, reaction mechanisms, and reactor hy-

drodynamic phenomena associated with the conversion of coal-derived synthesis gas to transportation fuels. Emphasis is placed on catalysts

and reactor systems that permit direct utilization of low H_2/CO ratio synthesis gas while at the same time improve the selectivity of the product to gasoline and distillate range hydrocarbons. This effort includes the evaluation of catalyst preparation and activation procedures that may influence activity, product selectivity, and stability during catalytic conversion of synthesis gas; the description of bulk and surface chemical/structure features of catalysts that relate to catalyst formation and use; the application of appropriate methodology for analysis of indirect liquefaction products; and finally, the investigation of hydrodynamic phenomena in nonreacting model systems to provide a sound basis for the design of slurry bubble column reactors.

This quarter, a series of experiments was conducted with the Fischer-Tropsch catalyst, Co, and zeolite catalyst, HZSM-5, combined in different ways. The objective of this set of experiments was to elucidate the source of methane when synthesis gas is converted to aromatics over intimate mixtures of Co and HZSM-5. Hydrogenolysis of light alkanes was identified as one possible source.

Work continued on developing a gas chromatographic method for the analysis of the organics present in the aqueous portion of the FT product. A bonded-phase (Carbowax 20M) fused-silica capillary column gave virtually base-line resolution of the alcohols, acids, ketones, and esters present in the aqueous phase.

X-ray photoelectron spectroscopy measurements of precipitated Fe-Cu catalysts indicated that during H_2 reduction, Na present in the material concentrates on the surface of the catalyst. The concentration of Na on the surface increases with increasing H_2 exposure time.

An experimental program has been completed for critical gas velocities required to achieve complete suspension of the solids in a slurry bubble column. Axial solids concentration distributions have been measured below and above the critical gas velocity for water and aqueous ethanol liquid systems.

Synthesis Gas Chemistry

V.U.S. Rao, Cost Account Manager

***B.D. Blaustein, Chief,
Process Sciences Division***

The objective of the program is to obtain a thorough fundamental understanding of catalyst systems that permit direct utilization of low H_2/CO ratio synthesis gas while simultaneously

improving the selectivity of the product to gasoline and distillate range hydrocarbons. Certain intrinsic properties of the catalyst and the support play very important roles in determining catalytic conversion and selectivity. These include (1) metal crystallite size (i.e., degree of dispersion), (2) the pore size distribution of the catalyst and the support, (3) metal-support interactions, (4) presence of promoters in the catalyst, and (5) presence of a shape-selective phase (e.g., zeolite) in the catalyst. There is considerable interest in examining catalysts that can be utilized in a slurry-phase or a bubble-column reactor. Among the advantages of a slurry-phase reactor are minimum carbon formation on the catalyst and low methane yield. Typical catalysts, such as precipitated iron and Fe-Mn, are being examined in the slurry-phase to establish the relationships between preparative and activation procedures, and conversion and selectivity. Shape-selective catalysts such as ZSM-5 to which a Fischer-Tropsch element such as cobalt has been added can perform a single-step conversion of synthesis gas to high octane gasoline components. Such a conversion can also be performed in a two-stage reactor with the FT element in the first stage and the shape-selective component in the second stage. It is of interest to contrast the reaction pathways in the two cases. Experiments will be performed in an effort to elucidate the possible role of olefin interception in affecting the selectivities of bifunctional catalysts.

Preliminary data reported in the previous quarter indicated that preparation of precipitated iron catalysts using a batch procedure (addition of a solution of sodium carbonate to an iron nitrate solution) was as effective as the continuous flow in-line mixing technique to prepare catalysts with high olefin selectivity. More complete data on the selectivity of these catalysts are reported in Table 26. It is apparent that low pH results in high olefin selectivity regardless of the preparative procedure. The addition of copper results in a slightly less olefinic product, although thermogravimetric data indicate the importance of copper to effect complete activation of the catalyst (i.e., catalysts not containing copper showed low activity). Copper was incorporated into these catalysts in amounts of 1 wt% to 3 wt% by impregnation of the dried catalyst with a copper nitrate solution.

It has been established that residual soda (from the use of sodium carbonate as the precipitating agent) contributes to carbon deposition, with a resulting loss of activity. Consequently, three catalysts were prepared with ammonium hydrox-

Table 26.
Selectivities of Precipitated Iron Catalysts in Syngas Conversion.

Preparation	Olefin/Paraffin (C ₂ -C ₄)	Preparation	Olefin/Paraffin (C ₂ -C ₄)
3.5 C	7.1	3.5 C (Cu)	7.4
3.75B	6.9	3.75B (Cu)	5.1
5.95B	6.5	5.95B (Cu)	5.8
7.65C	4.0	7.65C (Cu)	3.7

C - continuous.

B - batch.

Number preceding B or C is pH.

(Cu) indicates promotion with copper.

ide instead of sodium carbonate using the continuous flow procedure. The microreactor selectivities are reported in Table 27. There appears to be no trend involving pH and selectivity, as was found to be the case when using sodium carbonate. In addition, the presence of copper results in a large decrease in olefin selectivity, in contrast to that observed in the case of sodium carbonate. Good activity maintenance was observed for preparations 6.2 and 7.6, while the activity of preparation 8.9 decreased continuously over a two-week period. As expected, carbon deposition on these catalysts was minimum. Pore size distribution data on the carbided catalysts are in agreement with the observation previously reported by Dry, namely, the average pore diameter increases with the use of NH₄OH as the precipitating agent. Thus the slow rate of deactivation of catalysts 6.2 and 7.6 may be due to either a low rate of carbon deposition or the absence of pore blockage due to wax accumulation. The poor activity maintenance of preparation 8.9 is puzzling, however.

Further chemical and thermomagnetic characterization of a coprecipitated iron-manganese slurry phase catalyst was conducted during this quarter. The catalyst composition as measured by atomic adsorption analysis was 13.4 wt% Fe and 49.8 wt% Mn, confirming the nominal preparation ratio of 20 Fe/80 Mn. Sequential dehydration, air-oxidation, and hydrogen-reduction treatments of the catalyst indicated that 63% of the manganese was in the Mn⁺³ oxidative state, with the balance as Mn⁺². The XRD measurements showed the material to consist of a spinel-type phase similar to FeMn₂O₄. The Fe in the spinel phase is inactive

Table 27.
Selectivities of Precipitated Iron Catalysts Prepared by Using Ammonium Hydroxide as the Precipitating Agent.

Preparation (pH)	Olefin/Paraffin (C ₂ -C ₄)
8.9	4.4
6.2	4.5
7.6 Cu	1.9 → 3.3 (over a two-week period)

toward syngas conversion and explains the lack of activity in H₂-reduced Fe-Mn samples. For carbon monoxide reductions performed in the TGA at low pressure, i.e., 0.3 atm CO, at temperatures in the range of 250°C to 275°C, the extent of reduction exceeded values expected for the total reduction of iron oxide to metallic iron. Thermomagnetic measurements also indicated that the Häag carbide Fe₅C₂ was formed in all but the low temperature (250°C), short-time (4-hr) reductions. These observations pointed to the conclusion that treatment with CO alone partially reduced the manganese oxides within the catalyst.

Activation studies in the slurry phase with a 20 Fe/80 Mn catalyst continued during this quarter. The effects of activation temperature, pressure, and procedure on catalyst activity, selectivity, and stability were investigated. Synthesis results were compared with a base-line catalyst activation that was performed with carbon monoxide at

275°C, 200 psig, and 2.25 WHSV. A low pressure activation had the most noticeable results. After activation at 275°C and 0 psig, helium was introduced to pressurize the system to synthesis pressure (200 psig). The ($H_2 + CO$) conversion was 5 mole percent greater than the base case and was relatively stable, since conversion only declined 5% over the first 200 hours of operation. However, the product selectivity was similar to the base case: hydrogenation of the primary olefins with time on stream occurred along with olefin isomerization reactions.

A test was made with the 20 Fe/80 Mn catalyst that had been activated in carbon monoxide at a higher temperature (300°C). Catalyst activity decreased immediately upon introduction of synthesis conditions. In another test, a Kölbel type activation was performed: carbon monoxide followed by hydrogen. The ($H_2 + CO$) conversion was 5 mole percent lower than the base-line test, but the product selectivity was again similar to the base-line test: an increase in hydrogenation of olefins with time and an increase in olefin double bond isomerization. Slurry samples were withdrawn at various times on stream, and analytical surface techniques will correlate catalyst properties with catalyst activity, selectivity, and stability.

The Fischer-Tropsch reaction with pressed pellets of 20 Fe/80 Mn catalyst was also inves-

tigated in a gas phase backmixed reactor. After catalyst stabilization, process parameters were varied and data obtained were used with a simple kinetic model assuming a first-order dependence on hydrogen. Kinetic constants obtained at different temperatures led to an observed activation energy of 14 kcal/mole, which is low, probably due to pore diffusional limitations in the catalyst pellet. However, selectivity trends with time and varying process parameters were the same as the iron-manganese catalyst in the slurry phase operation.

Recent experiments have given interesting information comparing the Fischer-Tropsch (FT) synthesis over a FT-ZSM-5 combination catalyst with that conducted in two steps over separated FT and ZSM-5 catalyst beds. The FT catalyst tested was 14.4% precipitated cobalt physically admixed with Davison 952 silica. The conversion and selectivity of this catalyst are shown in the first column of Table 28. The second column shows the results for the same FT catalyst in the first stage and HZSM-5 in the second stage. Both stages are at 280°C. In this case, ethylene, propylene, and butene are nearly totally involved in the production of aromatics, either as the building blocks in the oligomerization step or as the hydrogen acceptors in the aromatization step, where they would be converted to C_2 - C_4 alkanes. The increase in the yield of C_3 and C_4 alkanes is notice-

Table 28.
Conversion of Synthesis Gas in a Microreactor
 $H_2/CO = 1$, $P = 21$ atm, $T = 280^\circ C$, $WHSV = 0.77$

Catalyst	Co	Co (1st stage) ZSM-5 (2nd stage)	Co + ZSM-5 (single stage)
CO conversion (%)	49.7	51.7	47.1
H_2 conversion (%)	79.8	80.5	83.0
HC Product (wt%)			
CH_4	13.8	14.0	24.9
C_2H_4	0.2	0.1	0.2
C_2H_6	3.2	3.6	3.0
C_3H_6	4.8	0.0	0.4
C_3H_8	1.9	6.0	3.4
C_4H_8	2.5	0.0	0.9
C_4H_{10}	1.5	11.0	8.3
C_{5+}	72.1	65.2	58.9
Liquid Product (wt%)			
Aromatics	3	33	35
Olefins	34	8	12
Saturates	63	59	53

able, while the methane production is unchanged. The third column shows the results for the FT catalyst mixed with 50% silica and 50% HZSM-5 in a single stage. Of interest is the sharp increase in methane produced, while the wt% aromatics is nearly the same as in the two-stage experiment. This suggests that a secondary reaction, possibly hydrogenolysis, is occurring over cobalt, resulting in the formation of additional methane from ethane, propane, or butane. The yield of C_2 - C_4 alkanes is lower in this instance than in the two-stage experiment, thus supporting this possibility. This type of side reaction would only be enhanced in the single-stage experiment, where the additional light paraffins can react over the cobalt particles in intimate contact with HZSM-5.

In the next quarter, catalyst activation studies with the iron-manganese catalyst will continue. An effort will be made to stabilize the catalyst and to increase the olefin content of the light gas produced by adding potassium promoter to the catalyst system. The precipitated iron catalysts will be examined using differential scanning calorimetry. Microreactor studies will be conducted on Ru- and Co-exchanged controlled-pore glass catalysts prepared at Sandia National Laboratory. Construction of the temperature programmed desorption apparatus was completed during the quarter. After an initial equipment shakedown and calibration period, the apparatus will be used to study the competitive surface adsorption of CO and H_2 on the Co-ThO₂-ZSM-5 catalyst system. These studies will be made with the objective of gaining insight into possible modifications of the catalyst leading to lower methane yield and a higher yield of other FT products. Experiments will be performed to investigate in detail the role of hydrogenolysis of C_{2+} alkanes in contributing to methane formation in syngas conversion over metal-zeolite catalysts.

Product Characterization

G.A. Gibbon, Cost Account Manager

**H.L. Retcofsky, Chief,
Analytical Chemistry Branch**

The objective of this report is the detailed qualitative and quantitative analysis of the liquid and solid (wax) products of the Fischer-Tropsch reaction. The composition of these materials can vary widely depending on the catalyst used, catalyst age, and reactor conditions. Thus, the development of such analyses is crucial for an understanding of the chemistry that occurs in the FT process.

The use of multitechnique analysis during FY83 identified the best techniques to be used for certain types of products. This experience and knowledge will be used during FY84 to select one or two product analysis techniques for providing quantitative information on the products from slurry phase catalysis. More rapid data work-up procedures, including automation of the IR matrix calculations and specialized computer programming for the GC analysis, will also be used to decrease the turnaround time for product analysis. Such an enhancement in turnaround time will give more timely information concerning reactor conditions and/or catalysts to be further investigated to those researchers performing reaction studies and catalyst characterization.

During the past quarter, 82 samples were analyzed by the dual capillary column gas chromatographic method described in the last quarterly report. A manuscript describing the method has been submitted for internal review before its submission to Analytical Chemistry. Work has continued on improving the computer software used in the method, with the goal of eliminating completely the need for interaction with the analyst. This is an important step in our objective of installing the method as an automated, on-line analysis.

The task of developing a gas chromatographic method for the analysis of the organics present in the aqueous portion of the FT reaction product is on schedule. A bonded-phase (Carbowax 20M) fused-silica capillary column gives virtually baseline resolution of the alcohols, acids, ketones, and esters present in such materials. Injection (split, splitless, and on-column) and quantitation (internal standard and standard addition) procedures are now being evaluated. Method development should be completed in the next quarter. When the method is ready for routine use, PETC will have the ability to analyze all four product streams of the FT reaction: gases, liquid product, wax product, and organics in the product water.

Catalyst Characterization

J.M. Stencel, Cost Account Manager

**H.L. Retcofsky, Chief,
Analytical Chemistry Branch**

The goal of this project is to ascertain structural and chemical properties of indirect liquefaction catalysts that correlate with their activity, selectivity, and stability. Surface-sensitive and bulk-characterization methods, in conjunction with in situ techniques, will be utilized in a con-

certed effort to describe those features of catalysts that relate to the production of liquids during catalytic coal liquefaction.

This quarter, X-ray photoelectron spectroscopy (XPS) measurements of the surface concentrations and elemental speciation in H_2 -reduced, precipitated Fe-Cu catalysts were begun. These measurements show that Cu facilitates the reduction of Fe_2O_3 to Fe metal at $275^\circ C$. During these H_2 reduction experiments, the concentrations of Na on the surface of the catalysts increased with increasing H_2 exposure times. The Na is either in the form of NaOH or $NaHCO_3$, the origin and concentration of which are under further investigation. The iron is not observable with XPS in the two catalysts that have been exposed to 1:1 syngas for 16 hours at $275^\circ C$, whereas significant concentrations of C, Na, and Cu are observable with XPS.

The ion scattering spectrometry (ISS) measurements on H_2 and CO activated Fe-Cu catalysts were also continued this quarter. These measurements show that the concentration of Na within 0.5 nm of the surface is greater for samples containing 27-nm pores than for samples containing 14-nm pores. The bulk concentration of Na in samples containing 14-nm pores is five times greater than that for the sample containing 27-nm pores. Hence, the difference in Na surface concentration is opposite of that expected from the bulk Na concentration.

Preliminary XPS measurements on the H_2 reducibility of 20 Fe/80 Mn also began this quarter. These measurements show that Fe in this catalyst does not reduce to metallic Fe at temperatures from $250^\circ C$ to $450^\circ C$. Instead, the changes observed in the XPS spectra after H_2 exposure suggest that a spinel, $FeMn_xO_y$, has formed. This formation coincides with a decreased Fe surface concentration relative to the Mn concentration.

Next quarter, studies of the reducibility of Fe in Fe/Mn and Fe-Cu catalysts will be continued. In addition, surface speciation and elemental concentrations as a function of H_2 and $H_2 + CO$ exposure on Fe-Cu and Fe/Mn catalysts will be investigated more thoroughly.

Slurry Bubble Column Reactor Studies

D.N. Smith, Cost Account Manager

J.A. Ruether, Chief,

Coal Conversion Engineering Branch

In Fischer-Tropsch (F-T) reactions conducted in a slurry phase, transport parameters play a large

role in determining global reaction rates and, quite likely, selectivities. The characterization of in situ hydrodynamics therefore becomes an integral part of the total design of F-T reactors. It is the purpose of this work to provide a reliable data base for some of the important reactor parameters that contribute to the understanding of F-T reactor performance. To accomplish this, several transport properties, such as gas hold-up, bubble size and velocity distributions, and absorption coefficients, will be measured in organic liquids having bulk transport properties similar to those of F-T reactor fluids. The measurements will be compared, to the extent possible, to transport coefficients obtained in an F-T reactor.

During this quarter, approximately 95% of the construction of an 0.87-in.-i.d. by 36-in.-long, hot, pressurized bubble column has been completed for measuring bubble size, velocity, and hold-up with an in situ microprobe. A molten paraffin wax will be used as the liquid phase for shakedown tests. The liquid transport properties (i.e., density and viscosity) are currently being measured as a function of temperature. A robust design has been developed for the miniaturized impedance probe that will allow for operating temperatures and pressures of $260^\circ C$ and 300 psig. The probe wires are coated with a high temperature ceramic cement and silicone lacquer. The lacquer will permit operation of the probe in aqueous vapors as well as in paraffinic liquids. An alternating current circuit has been designed to permit detection of capacitance/conductivity changes between the liquid and gas phases. The heart of the probe circuit is an impedance bridge that contains the probe circuit on one leg of the bridge. Shakedown testing of the hot model is expected to begin early next quarter.

An experimental program has been completed for critical gas velocities required to achieve complete suspension of the solids in a slurry bubble column. Axial solids concentration distributions have been measured below and above the critical gas velocity for water and aqueous ethanol liquid systems. A report on the findings from this study is currently being prepared for submission to the AIChE J. A criterion for complete suspensions of solids has been developed that depends on the length and diameter of the column, superficial velocities, and hindered-settling velocity.

Another report has also been prepared based on an experimental investigation of axial solids concentration distributions in a slurry bubble column with polydispersed solids. This report looks at the effect of particle size distribution that is commonly encountered in the operation of an in-

dustrial slurry reactor. Significant findings are that the mean particle size does not determine the solids concentration distribution and, furthermore, that the presence of large particles (particle size greater than 150 μm) greatly influences the solids concentration distribution, especially near the bottom of the column.

For the next quarter, construction and shakedown testing of the 0.87-in.-i.d. bubble column will be completed. Testing of the miniaturized probe will begin in the hot model. Also, an experimental program will be started for measurements of volumetric liquid-side mass transfer coefficients in organic slurries.

SURFACE GASIFICATION

R.M. Kornosky, Coordinator

The objectives of the surface gasification studies are to provide experimental data that will enhance the understanding of various phases of the gasification process, resolve many of the serious technical problems that may hinder the movement toward commercialization, and advance the state-of-the-art.

In an attempt to describe flow-regime transitions in a gas/solid fluidized bed at elevated pressure, a series of experiments was performed in which pressure fluctuations within the fluidized bed are measured as functions of various operating parameters. The data will be statistically analyzed to derive a correlation between pressure fluctuation and flow-regime transition.

The separation of hydrogen and methane mixtures by adsorption on activated carbon can be an effective means of gas purification in advanced coal conversion processes. Experimental data describing the adsorption of hydrogen and methane mixtures on commercially available activated carbons were correlated and interpreted by three predictive theories: the ideal adsorbed solution, a modified Polanyi potential theory, and the loading-ratio correlation. Results showed that for over the range of temperatures and pressures investigated, none of the predictive methods offered better agreement when compared to the experimental data. However, the loading-ratio correlation is the only non-iterative method, which makes it much simpler to use.

The 36-stage, countercurrent, liquid-liquid extraction column was operated successfully with a coal gasification process wastewater. Experimental data from this apparatus will provide column design information and operating conditions that enhance contaminant removal.

Advanced Surface Gasification Support
D.C. Chitester, Cost Account Manager
J.A. Ruether, Chief,
Coal Conversion Engineering Branch

The objective of this project is to develop a data base for the effects of pressure on fluidization parameters, such as minimum fluidization velocity, complete fluidization velocity, bubbling-bed characteristics, particle elutriation and attrition, flow-regime transitions, and jet penetration distance. Experiments are being performed using two- and three-dimensional Plexiglas models. A 24-inch-diameter, high-pressure containment vessel capable of operating at pressures up to 1000 psig is being used to house the Plexiglas models. The containment vessel has 24 glass view ports to facilitate visual observation and allow photography of the fluidized bed with a high speed motion picture camera. Only two such units exist in the USA.

During this quarter, a series of bed expansion experiments using a two-dimensional model was completed. The variables in these experiments are outlined in Table 29. A high-speed recorder in conjunction with a differential-pressure transducer was used to record the bed-pressure drop and total pressure fluctuation at each gas velocity. Bed height at each velocity was also recorded. The velocities at which the following phenomena occurred were noted: minimum fluidization, complete fluidization, minimum bubbling, transition from bubbling to slugging, and transition from slugging to turbulence. High-speed photographs were taken at velocities of particular interest. Preliminary inspection of the data indicates that

Table 29.
Variables in Bed Expansion Experiments

Variable	Value
Pressure (kPa)	101, 1621, 3242, 6485
Superficial Gas Velocity (cm/sec)	0 - 122
Solids Density (gm/cc)	1.2 (coal), 2.5 (glass beads), 2.0 (alkalized alumina)
Solids Size	-50 + 140, -100 + 140, -100 + 200, -140 + 200, -140 + 270, -200 + 325 -50 + 270 mesh (glass beads) -20 + 100, -100 + 200, -200 + 325, -20 + 325 mesh (coal) 5 mm (alkalized alumina)

trends identified in previous work are followed. The data obtained from these experiments will be valuable in furthering the understanding of flow regime transitions and the voidage-velocity relationship in high-pressure fluidization.

A video system was obtained for use with the high-pressure model. It includes a high-resolution color video camera, a color monitor, and an industrial format VCR. The VCR offers a time-lapse feature that enables playback in slow motion equivalent to a movie camera operated at approximately 1000 frames-per-second. This system enhances the operability of the unit because the bed can be monitored continuously. Also it offers the ability to maintain a constant visual record of all experiments. The camera will be mounted on a motorized transport so the operator can change its position remotely, thus increasing operating efficiency. A second industrial format VCR is available for editing purposes, and a commercial format VCR (VHS or Beta) is being purchased for use in presentations.

The problems that existed in the transmission of data from the Biomation unit to the PDP 1140

1. Chitester, D.C., Kornosky, R.M., Fan, L.-S., and Danko, J.P., "Characteristics of Fluidization at High Pressure," *Chem. Eng. Sci.*, 39(2), p. 253 (1984).

computer in the pressure fluctuation-flow regime transition experiments were solved by the installation of a current-loop amplifier. The pressure fluctuation experiments-flow regime transition were then repeated. A complete set of data was obtained, which, upon inspection, was found to be accurate. These data will be statistically analyzed. Various statistical functions, including the probability density function, the cumulative distribution function, the auto- and cross-correlations functions, and the power spectral density function, will be examined to derive a correlation between pressure fluctuation and flow-regime transitions.

A paper entitled "A Generalized Methodology for Estimating Minimum Fluidization Velocity at Elevated Pressure and Temperature" was written jointly with Westinghouse Research and Development. The methodology proposed in the paper makes use of the general Barnea-Mizrahi correlation² for fluidization and sedimentation of multiparticle systems. This correlation is based on a discrete particle model and is thus fundamental in nature. This correlation is combined with drag

2. Barnea, E., and Mizrahi, J., "A Generalized Approach to the Fluid Dynamics of Particulate Systems, Part I. General Correlation of Fluidization and Sedimentation in Solid Multiparticle Systems," *Chem. Eng. J.*, 5, p. 171 (1973).

correlations proposed by Clift et al.³ to provide a basis for the methodology. This paper was accepted for presentation at the AIChE 1984 Annual meeting, November, 1984, San Francisco, Calif. It will also be submitted to AIChE Journal for publication.

A series of experiments was completed using colored particles and special photographic techniques to study local bed voidages and particle velocity distributions. The following conclusions were drawn from these experiments: (1) at the region near the distributor, the particles are more heterogeneously distributed than at the region near the upper part of the bed; (2) voidage fluctuation is more pronounced with larger particles; (3) although past researchers have stated that wave propagation requires a deep bed,⁴ propagation does indeed occur in a shallow bed; and (4) for a given large average voidage, large particles possess a higher velocity or speed than do smaller particles. A paper is now being written jointly with Ohio State University detailing the results of these experiments, and it will be submitted to Chemical Engineering Communications for publication.

A paper entitled "A Photographic Analysis of High Pressure Fluidization Phenomena" was published as a DOE Topical Report. The paper includes a qualitative description of high-pressure fluidization accentuated by illustrations of particularly interesting phenomena.

Under contract to PETC, Dr. R.T. Yang, State University of New York at Buffalo, completed a study to analyze and correlate the PETC data base describing the adsorption of hydrogen and methane mixtures on three commercially available activated carbons. Such a separation process is, in principle, less energy-intensive than presently used high-purity processes (liquefaction and molecular sieves). Although lacking in selectivity, adsorption on activated carbon may be the best method for the separation of hydrogen and methane in advanced coal conversion processes. In this study, the equilibrium adsorptions of hydrogen and methane from their mixtures were measured by analyzing the breakthrough curves of the more strongly adsorbed methane at various temperatures and pressures that are

3. Clift, R., Grace, J.R., and Weber, M.E., *Bubbles, Drops, and Particles*, Academic Press, New York (1978).

4. Jackson, R., *Trans. Inst. Chem. Engrs.*, 41, p. 12 (1963).

suitable for application in coal conversion processes. The experimental data were further correlated and interpreted by three predictive theories: the ideal adsorbed solution, a modified Polanyi potential theory, and the loading ratio correlation. Results showed that for over the range of temperatures (78°F to 400°F) and pressures (atmospheric to 1000 psig) investigated, none of the predictive methods offered better agreement when compared to the experimental data. However, the loading ratio correlation is the only non-iterative method, which makes it much simpler to use. The complete results of this study are presented in a manuscript entitled "Adsorption of Gas Mixtures on Activated Carbon," which was accepted for publication in Carbon.

In the next quarter, another series of pressure fluctuation-flow regime transition experiments will be conducted as an extension of the previously conducted series of experiments.

Treatment of Coal Gasification Wastewaters

R.P. Noceti, Cost Account Manager

*B.D. Blaustein, Chief,
Process Sciences Branch*

The objectives of this program are to assess treatment requirements and develop environmental control strategies for wastewaters produced in coal gasification processes in order to ensure the availability of effective and economical environmental controls.

During this fiscal year, work is being performed in the following areas:

A. Westinghouse Wastewater Stream Stripping

Westinghouse gasification process wastewater contains low concentrations of organic contaminants and moderate concentrations of ammonia, sulfide, thiocyanate, and cyanide. In this project, a bench-scale steam-stripping apparatus will be employed to determine the feasibility of removing ammonia, sulfide, cyanide, organic compounds, and other contaminants from this wastewater to levels acceptable for reuse or discharge to the environment. This would provide a simple wastewater treatment system employing steam stripping as the sole treatment operation. During this quarter, minor modifications to the H₂S adsorption system and final shakedown operations have been completed. The free-leg stripping study will begin in July.

B. Solvent Extraction

In this study, a 36-stage, counter-current, liquid-liquid extraction column will be used to complete an investigation of the solvent extraction of coal gasification process wastewaters with the objectives of obtaining design information and of determining operating conditions that improve the removal efficiency of the process. Column throughput and sizing information will be obtained, and an evaluation of the effect of solvent recycle on column efficiency will be made.

During this quarter, the solvent extraction column was operated successfully over solvent-to-

water ratios of 0.01 to 1.00 with a total liquid throughput of 200 mL/min. During the next quarter, while operating at a fixed solvent-to-water ratio of 0.1, the total liquid throughput will be varied from 50 to 300 mL/min and chemical analyses of the raffinate will be completed.

C. Technology Transfer

A paper, "Biochemical Oxidation of Solvent Extracted Coal Gasification Process Wastewater," was presented at the Los Angeles national meeting of the American Society of Civil Engineers Environmental Engineering Division in June.

ANALYTICAL CHEMISTRY SUPPORT

H.L. Retcofsky, Coordinator

Analytical chemistry support at PETC involves a variety of functions, including the following:

- development and application of advanced analytical techniques and methodologies for the solution of problems associated with the utilization and conversion of coal.

- responsibility for the analytical support to the Center and to other organizations engaged in coal research and utilization. This also includes quality assurance responsibility for services performed by non-federal contractor laboratories.

- the dissemination of information as it relates to the analysis of coal and to the characterization of process streams associated with coal conversion.

- the preparation and dissemination of Hardgrove Grindability Index Standards. PETC is the world's only source of these standards.

During the past quarter, the second issue of Synfuels Characterization was printed and distributed, and PETC's quality assurance program for coal analysis was fully documented. Included among the rather special samples analyzed this quarter were samples of fly ash to assess attrition levels in a flue gas cleanup process, and a large number of samples from the thermal hydrogenation tests with the Wilsonville thermal resid. A second ASTM D-1160 distillation apparatus was constructed and is now in operation to meet increased demand for the procedure. Several contracts for outside analytical services were extended, and a new contract for specialized inorganic analyses is in preparation. An interface between

the gas chromatography laboratory's data acquisition system and the Branch's laboratory information management system was completed, resulting in the complete automation of both technical and managerial reporting.

Analytical Support

H. Schultz, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objectives of this project are to (1) conduct analytical chemical research relevant to the Center's mission, (2) provide special analytical services, (3) develop new and improved analytical chemical methods for materials derived from coal, and (4) perform standardized chemical and physical analyses on coal and coke in support of government research programs and coal purchases.

Construction of the second vacuum system and distillation apparatus for ASTM D-1160 low-pressure distillations has been completed, and the system has been put into service. As a result of the construction of the second system, efficiency has been doubled.

A shipment of coal has been received for use in the preparation of Hardgrove Grindability standards. The coal is prewashed and double-screened to ensure the quality of these standards that are only available from PETC. Twelve sets of the standards were shipped during the quarter to foreign and domestic users. The standards are used to calibrate equipment.

Contracts for water analysis, D-1160 distillations and ultimate analyses, and microanalysis have each been extended for one year so that continuous service in these areas will be provided to PETC researchers.

A contract is being prepared for performance of Total Inorganic Carbon, Total Inorganic Sulfur, Silicon, and Metals Analyses. When the contract is awarded, backlogs on analyses requested, which were due to shortages of personnel, should be partially relieved.

On June 12, high priority samples of fly ash were received. The fly ash originated in the baghouse and the preheater of the 500 lb/hr Solid Fuel Combustion Test Facility. All samples were analyzed for copper, and the results were reported to the Flue Gas Cleanup Conference in Washington, Pa., the same day that the samples were received. Results were used to assess the degree of attrition of the sorbent in the CuO flue gas cleanup process.

During the quarter, analyses were completed on 729 coal samples, of which 531 were performed at a commercial laboratory under contract to PETC. Analysis requests totaled 1449 during the quarter, and 1300 analyses were reported on non-coal samples. Forty-three samples of coal were received from, and 81 samples of coal were sent to, commercial testing laboratories during the quarter as part of PETC's quality assurance program.

A document describing in detail the quality assurance program employed at PETC in the analysis of coal by ASTM procedures has been completed. Included are sections on Actions Taken by PETC, Actions Taken by the Contractor, and Actions Taken by Both PETC and the Contractor to ensure quality.

Difficulties were experienced with the ability of the automatic ash fusion system to detect the correct number of cones present in the ash fusion furnace. Numerous contacts with the manufacturer did not successfully resolve the problems, so the matter was referred to PETC procurement on June 12 for action.

On May 16, 1984, J. Shremshock and R. Welsh of PETC met with representatives of the Department of Defense (DOD) at the Defense Fuel Supply Center in Alexandria, Va., to discuss coal analyses performed at PETC for DOD. The PETC representatives presented evidence of sampling problems at two DOD bases. As a result of the meeting, PETC has volunteered to perform reana-

lyses on certain coal samples. In addition, it was agreed that the PETC Coal Analysis Laboratory will not process any sample where (1) the sample is not in a container provided by PETC, (2) the container is damaged in shipment, and/or (3) the numbers on the containers do not agree with the numbers on the sampling form that accompanies each shipment.

During the next quarter, the problems with DOD coal samples will be resolved; Quality Assurance documents for other support analyses will be completed; and the contract for outside analytical services will be completed and delivered to Procurement.

Spectroscopic Support

R.G. Lett, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective is to provide specialized analytical support to research projects at the Pittsburgh Energy Technology Center. This encompasses both qualitative and quantitative analyses by spectroscopic and spectrometric techniques, and the development or evaluation of new analytical procedures based on these techniques for applicability to coal conversion products and related materials.

Last quarter, approximately 600 analyses were performed in-house. This represents a 50% increase over the support work load in recent quarters and results from an increased demand for analyses by the direct liquefaction and PCT properties programs. The other major user of spectroscopic support services continues to be the indirect liquefaction program. In addition to in-house analyses, eight field ionization mass spectrometry profiles of fractions from the PETC fractional distillation unit were obtained from an outside contractor.

About one quarter of the analyses performed were on solvents, feed slurries, and products from a series of thermal CSTR hydrogenation tests with Wilsonville SRC at 720°F and 750°F under 2000 psi H₂. The total samples and distillate fractions (<650°F, 650°F — 850°F, >850°F) were analyzed by ¹H nuclear magnetic resonance for evidence of any hydrogen redistribution and by near-infrared spectroscopy for any changes in heteroatom (OH, NH) functionality.

To assist in resolving questions concerning operation of the Wilsonville critical solvent deasher (CSD) unit with subbituminous coal-

derived feed, the CSD feed, the first-stage settler overheads, the second-stage overheads, and the ash concentrate are being analyzed to determine any physical or chemical differences between the process streams with respect to ash characteristics. Elemental and X-ray diffraction data indicate no significant differences in ash or mineral matter composition of the CSD feed and product streams. Possible differences in mineral particle-size distribution are being investigated by scanning electron microscopy.

Next quarter, experimental priorities will include characterization of pseudocomponent fractions from projects in the Thermophysical Properties Program. The aromaticity and chemical functionality of vacuum bottoms fractions from the PETC fractional distillation unit will be determined, and chromatographically separated saturate, aromatic, acid, and base fractions from narrow-boiling-range distillation cuts analyzed. Documentation of the PETC custom electron spin resonance data system and procedures developed for infrared functional group type analyses will be completed.

Instrumentation Support

G.A. Gibbon, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The primary purpose of this project is to supply instrumental support and analytical method development to Pittsburgh Energy Technology Center personnel involved in process development research. For example, during the coming year, an on-line, automated gas chromatograph will be installed on the reactors operated under the cost account entitled "Fundamental Studies of Coal Conversion Catalysis." A second objective is to

provide computerized data acquisition, sample management, and automation services to the Analytical Chemistry Branch. In addition, the analytical needs of other researchers are reviewed and revised at regularly scheduled meetings with these researchers.

During the past quarter, 709 samples were submitted for gas analysis; 707 were reported and there is no backlog. For the same period, 63 samples were submitted for simulated distillation by gas chromatography; 63 were reported and the current backlog is 0.

The data acquisition system of the Branch's gas chromatography laboratory has been interfaced to the Branch's Laboratory Information Management System. Thus, the tracking of samples through the laboratory, the reporting and archiving of sample data, and the recording of productivity and backlog data are now fully automated.

The second issue of Synfuels Characterization was published in April. The issue features articles on Oil Shale Analysis, the Storage Stability of Light Coal-Derived Distillates, the Characterization of Coal Liquefaction Products by Vacuum Distillation, and the Availability of Samples from the Wilsonville Advanced Coal Liquefaction Facility.

The mass spectrometric method for the analysis of organics in FT product waters has been reviewed and revised. Included in the revision is the use of a heated-inlet system to assure complete vaporization of the entire sample into the spectrometer.

During the coming quarter, installation of the on-line GC will be started. In addition, a review of the on-line GC requirements of the indirect liquefaction project will be held with key project personnel.

PUBLICATIONS AND PRESENTATIONS

Title	Author(s)	
SRC Fuel for Oil-Designed Boilers: Test Results	G.T. Bellas Y.S. Pan R.B. Snedden J.I. Joubert	Proceedings of Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, Calif., May 11-13, 1984
Acid Rain	B.D. Blaustein	Presentation to Faculty and Students, Washington & Jefferson College, Washington, Pa., April 10, 1984
Chemistry of Coal Liquefaction	B.C. Bockrath	Presentation to Pennsylvania State University Faculty and Students, University Park, Pa., May 17, 1984
Coal Conversion and Hydrogen Utilization	B.C. Bockrath	Presentation at AR&TD Contractors' Review Meeting, Pittsburgh, Pa., June 6, 1984
PETC High Pressure Fluidization Cold Model - FY84 Project Review	D.C. Chitester	Presentation at the Proceedings of Fourth Annual METC Advanced Gasification Projects Contractors' Review Meeting, Morgantown, W.Va., June 1984
Biochemical Oxidation of Solvent Extracted Coal Gasification Process Wastewater	J.A. Cook C.J. Drummond R.P. Noceti J.G. Diskin	Presentation at and Preprints of the American Civil Engrs. National Conference on Environmental Engineering, Los Angeles, Calif., June 25-27, 1984
Coal Preparation: A Viable Approach to Sulfur Control	A.W. Deurbrouck	Presentation at Ohio University, Belmont, Ohio, May 15, 1984
Characterization and Comparison of Activities of Some Fe-Based F-T Catalysts	J.R. Diehl J.M. Stencel H.W. Pennline S.S. Pollack R.A. Diffenbach D. Fauth	Presentation at the 23rd Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Cleveland, Ohio, May 16-18, 1984
The Role of pH in the Preparation of Precipitated Iron Fischer-Tropsch Catalysts	R.A. Diffenbach D.J. Fauth R.R. Schehl J.M. Stencel J.R. Diehl	Presentation at the 23rd Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Cleveland, Ohio, May 16-18, 1984
Stack Contamination Effects During Small-Scale Combustion Testing of Synthetic Fuels	L.J. Douglas G.A. Gibbon C.M. White	DOE/PETC/TR-84/4, May 1984

*Non-DOE

Title	Author(s)	
Coal Gasification Wastewater Physicochemical Treatment Results: A Progress Report	C.J. Drummond	Proceedings of the Third Biennial Synfuels Wastewater Workshop, DOE/METC/84-5, March 1984
Coal-Water Methanol Slurries: Viscometric Properties and the Effects of Coal Type	A.C. Ekmann J.M. Ekmann	Presentation at the Sixth International Symposium on Coal Slurry Combustion and Technology, Orlando, Fla., June 25-27, 1984
Coal "Science"	D.H. Finseth	Presentation at the High School Science Workshop at Indiana University of Pennsylvania, Indiana, Pa., June 20, 1984
Combustion of Coal-Water and Petroleum Coke-Methanol-Water Mixtures in a Firetube Boiler	Y.S. Fu G.T. Bellas T.D. Brown J.I. Joubert	Presentation and Proceedings of the Sixth International Symposium on Coal Slurry Combustion and Technology, Orlando, Fla., June 25-27, 1984
Combustion of Coal-Methanol-Water Mixtures in a 700-hp Watertube Boiler	Y.S. Fu G.T. Bellas R.B. Snedden J.I. Joubert	Presentation at and Proceedings of the Sixth International Symposium on Coal Slurry Combustion and Technology, Orlando, Fla., June 25-27, 1984
On-Line Capillary Tube Viscometer for a Continuous Coal Liquefaction Unit	W. Fuchs M.L. Weiss D. Krastman R.M. Kornosky J.A. Ruether	Presentation at AIChE 1984 Spring National Meeting, Anaheim, Calif., May 20-23, 1984
The Behavior of the Slip Velocity and Its Relationship in Pneumatic Conveying	G.E. Klinzing* M.P. Mathur	AIChE Symposium Series on Fluidization and Fluid Particle Systems, June 1984
Raman Spectroscopic Investigation of the Effect of Hydration and Isotopic Exchange on Surface Tungstate and Molybdate in WO_3/Al_2O_3 and MoO_3/Al_2O_3 Catalysis	L.E. Makovsky J.M. Stencel R.J. Diehl P. Zandhius*	Presentation at the 23rd Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Cleveland, Ohio, May 18, 1984
Selectivity Aspects of F-T Conversion on Metal-Zeolite Catalysts	V.U.S. Rao R.J. Gormley R.R. Schehl A. Shamsi R.T. Obermyer* J.M. Stencel C. Bueno R.D.H. Chi T. Mentzer*	Presentation at Workshop on Zeolites and Molecular Sieve Materials in Heterogeneous Catalysis, held at Argonne National Laboratory, Argonne, Ill., June 21 & 22, 1984

*Non-DOE

Title	Author(s)	
Recent Developments in Indirect Liquefaction	R.R. Schehl	Proceedings of 12th Biennial Lignite Symposium: Technology and Utilization of Low-Rank Coals, W.R. Kube et al., eds., DOE/METC/84-13, Vol. 2, Feb. 1984, pp. 646-667
DOE Indirect Liquefaction Program	R.R. Schehl	Presentation at Ninth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, Calif., May 8-10, 1984
Separation of Isotopically Substituted Compounds Using Capillary GC	K.T. Schroeder	Presentation at the American Chemical Society National Meeting, St. Louis, Mo., April 8-13, 1984
Precipitated Fe and Fe-Cu Synthesis Gas Conversion Catalysts: Characterization and Activity	J.M. Stencel R.A. Diffenbach	Presentation at the Tri-State Catalysis Meeting, Lexington, Ky., May 23, 1984
Studies of Aged Catalysts from the Wilsonville Direct Coal Liquefaction Test Facility	F.V. Stohl* H.P. Stephens* G.J. Stiegel R.E. Tischer	Presentation at Ninth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, Calif., May 8-10, 1984
Coal-Liquids Upgrading with Bimodal Ni-Mo/Al ₂ O ₃ Catalysts	R.E. Tischer G.J. Stiegel N.K. Narain D.L. Cillo	Presentation at the 23rd Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Cleveland, Ohio, May 18-18, 1984
A Fundamental Study of Filtration and Dewatering of Fine Coal	R. Venkatadri* S.H. Chiang G.E. Klinzing* J.W. Tierney* W.W. Wen	COAL PREPARATION: An International Journal, Vol. 1, No. 1, 1984
Fractional Destruction of Coal Liquefaction Products	R.P. Warzinski	Presentation at a Research Seminar at the Department of Chemical Engineering, University of Oklahoma, April 4, 1984
Fractional Destruction of Coal Liquefaction Products	R.P. Warzinski	Presentation at a Research Seminar at NIPER, Bartlesville, Oklahoma, April 4, 1984
Ten Years of Energy Research	R.P. Warzinski	Presentation to Students and Faculty at Waynesburg College, Waynesburg, Pa., April 16, 1984
Fractional Destruction of Residuum	R.P. Warzinski	Presentation at the AR&TD Liquefaction Contractors' Conference, Pittsburgh, Pa., June 5, 1984

*Non-DOE

Title**Author(s)**

Flow Characteristics and
Handling Properties of
Commercial Coal-Water Mixtures

D.J. Wildman
J.M. Ekmann

Presentation at the Sixth
International Symposium on Coal
Slurry Combustion and Technology,
Orlando, Fla., June 25-27, 1984

*Non-DOE