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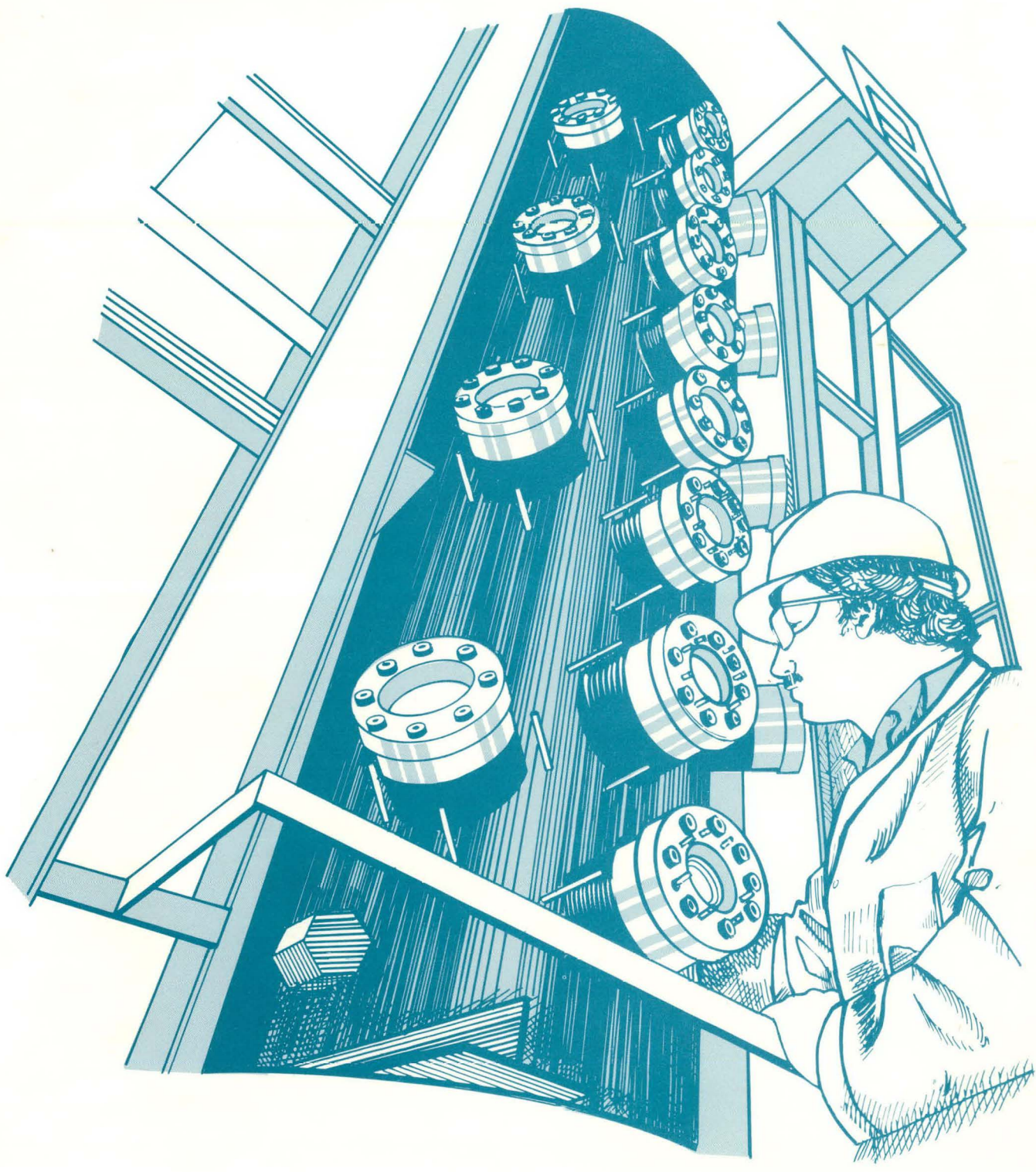
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DOE/PETC/QTR-84/1
(DE84008999)

Quarterly Technical Progress Report

Period Ending December 31, 1983



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



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**QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD ENDING
DECEMBER 31, 1983**

**April 1984
Date Published**

**Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

QUARTERLY TECHNICAL PROGRESS REPORT

October 1 - December 30, 1983

PETC/QTR -FY 84/1

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	1
PROJECT MANAGEMENT AND SUPPORT	3
Technical Support of Major Systems' Acquisitions	3
H-Coal Project Summary	3
SRC Technical Data Analysis	3
Physical, Chemical, and Thermodynamic Properties of Fossil Fuel Liquids	4
Wilsonville Process Development Unit	4
Component and Instrument Projects	5
Liquefaction Industrial Technology Projects	10
Indirect Liquefaction	10
Two-Stage Liquefaction	15
Disposable Catalysts	19
Liquefaction Process Research and Technology Development	21
Refining and Upgrading	23
MHD Projects	25
Engineering Development	25
Supporting Research	26
Systems Engineering	27
Component Development and Integration Facility	28
Closed-Cycle Systems	28
Alternative Fuels Technology	28
Flue Gas Cleanup	30
Coal Preparation	32
Coal Characterization	32
Coal Beneficiation	34
Ancillary Unit Operations	37

Advanced Research Contracts	41
Reaction Chemistry	41
Exploratory Development	42
Catalysis and Kinetics	43
Indirect Liquefaction	44
Structure and Characteristics of Coal	45
Characteristics and Analyses of Coal-Derived Liquids	46
Gasification	48
Combustion	48
Environmental	49
Pulverized Coal Combustion	50
Synfuel Utilization	55
 IN-HOUSE RESEARCH AND DEVELOPMENT	 57
AR&TD: Direct Utilization	57
Dense-Phase Powder Characteristics	57
Flow Characteristics of Coal-Based Fuels	58
Combustion Characteristics of Cleaned and Micronized Coals	58
Technique Development for Slagging and Fouling Characteristics	59
AR&TD: Structural Aspects of Liquefaction	59
Structural Changes During Coal Dissolution	60
Structural Mobility of Treated Coals and Coal Slurries	61
Structural Definition of Synthetic Fuels	61
Liquefaction Bottoms Characterization	62
Vibrational Spectroscopic Studies of Coal Conversion Catalysts	63
AR&TD: Mechanistic Aspects of Liquefaction	64
Investigations of Hydrogen Utilization	64
Mechanism of Coal Liquefaction	65
Fundamental Studies of Coal Liquefaction	66
Fundamentals of Coal Liquefaction in the Presence of Water	66
AR&TD: Environmental Aspects of Fossil Fuel Combustion	68
Acid Precipitation Studies	68
Acid Rain Precursor Studies	69
Coal Preparation	70
Fine Coal Characterization	71
Pyrite Size Distribution	71
Chemical Coal Cleaning Studies	71
Selective Coalescence	73
Flotation and Dewatering	74
Fine-Size Coal Agglomeration	74
Utilization: Coal Combustion Cleanup Technology	74
PETC Combined Flue Gas Cleanup Support	75
Fossil Energy/Resource Conservation and Recovery Act Support	79

Utilization: Combustion Technology	80
700-hp Combustion Test Facility	81
100-hp Combustion Test Facility	81
Fuel Rheology Laboratory	83
Direct Liquefaction	89
Liquefaction Bottoms Fractionation	90
ASPEN Modeling	91
Transport Studies in Coal Liquefaction	91
Catalyst Preparation and Characterization	94
Fundamental Studies in Coal Conversion Catalysts	94
Indirect Liquefaction	103
Synthesis Gas Chemistry	103
Catalyst Characterization	106
Product Characterization	106
Slurry Bubble Column Reactor Studies	107
Surface Gasification	108
Advanced Surface Gasification Support	108
Treatment of Coal Gasification Wastewaters	110
Coal Flow Test Facility	111
Analytical Chemistry Support	112
Analytical Support	112
Spectroscopic Support	113
Instrumentation Support	114
PUBLICATIONS AND PRESENTATIONS	115

EXECUTIVE SUMMARY

Sun W. Chun, Director

As the new fiscal year gets underway, considerable activity is taking place in PETC's coal preparation and flue gas cleanup programs in the wake of the high degree of industrial interest in research related to acid rain. Several new initiatives were begun in coal preparation during this quarter, including a project to develop a liquid CO₂ coalescence process that will produce a superclean coal containing less than 1% ash. One preliminary test of this process cleaned an Upper Freeport run-of-mine coal, usually very difficult to clean, from 35% ash to 10% ash, and a second test enhanced a clean Illinois coal from 8% to 2% ash.

Another new project in this area is focusing on chemical coal cleaning for the removal of harmful trace elements, such as arsenic, lead, and zinc. A third new effort is addressing the mineralogical and petrographic study of changes in mineral matter after the coal has been subjected to microwave desulfurization. Attempts are being made to characterize these changes by examining a number of representative coal samples at several stages before and after microwave treatment. Additional details of these and other related projects can be found in the section entitled "Project Management and Support/Coal Preparation."

Milestones were reached in both of our major electron beam flue gas cleanup projects. The Research-Cottrell E-Beam/Spray Dryer Project is undergoing its final check-out inspection, and shakedown testing should begin in January 1984. The Ebara E-Beam/Ammonia Injection Project got underway with the review of a draft work plan and the ordering of equipment for installation at the E.W. Stout Plant in Indianapolis.

Also during this quarter, a series of four 100-hour copper oxide attrition tests were performed in a fluidized bed of the flue gas stream in PETC's Solid Fuel Combustion Test Facility. Initial results suggest an attrition rate of no more than 0.05%/hour. Testing of PETC's fluidized-bed copper oxide process for simultaneous SO₂ and NO_x removal continued in an attempt to identify the causes of and possible solutions to sorbent attrition. Once these tests are completed this year, exploratory testing will begin of a technique involving combined SO₂/NO_x removal from flue gas via spray dryer injection of sodium/aluminum based sorbents.

In the area of coal-water mixtures, our major industrial contracts are now approaching critical milestones. Most of the coals that had been selected for producing candidate slurries in our Combustion and Fuel Characterization of Coal-Water Mixtures Program were found to be poorly suited to our needs. For this reason, the Gulf Research and Development Company has begun to investigate twenty-one coals that CWM vendors consider good for our test program.

The parallel effort in Plant Equipment Selection and Performance at TRW, Inc., is also progressing. The low-pressure transfer system is essentially complete; test loop fabrication and installation are complete; approximately 95% of the high-pressure loop piping has been installed; and all major equipment has been delivered. Equipment and instrument calibrations will begin early next quarter.

The analysis of our in-house combustion testing of micronized coal-water mixtures in PETC's 700-horsepower oil-designed boiler has been completed. By reducing the coal particle size from 90% minus 200 mesh down to 87% minus 19 microns, the carbon conversion efficiency increased from a level of 96% to 98%. Combustion tests with a commercially available CWM showed that combustion air enriched to 23% oxygen reduced the needed air preheat temperature from 370°F to 200°F.

Combustion testing in a smaller 100-horsepower boiler using a CWM containing 61% micronized coal beneficiated to 2.5% ash demonstrated that a fuel of this type could be burned at full boiler load with no preheated combustion air. When the coal was cleaned to only 7.8% ash, the CWM would not burn at ambient air conditions and needed a preheated combustion air temperature of 316°F. Similarly, the carbon conversion and boiler efficiencies decreased significantly. Details of all our on-site activities in CWM combustion during this quarter can be found in the section "In-House Research and Development/Utilization: Combustion Technology."

In the MHD Program, TRW, Inc., completed the fabrication of all components for the 50-MW(t) first-stage slagging combustor during this quarter. Hardware assembly, leak testing, and flow calibrations were completed, and all first-

stage hardware was installed at TRW's Capistrano Test Site. A detailed test plan was also completed.

After the completion of combustion tests at Capistrano, the TRW combustor will be shipped to the Component Development and Integration Facility (CDIF) in Butte, Montana. The necessary modifications to permit installation of the combustor later this year will begin at the CDIF during the next quarter.

Work also got underway in the new projects selected last summer to investigate advanced direct liquefaction processes. At Kerr-McGee, three scoping runs on their 350 pound/day integrated bench-scale unit were successfully completed. The objective of these runs was to evaluate subbituminous coal process options in terms of catalyst performance, distillate yields, and generation of coke precursors.

Cities Service began its project in the characterization of hydrogen donor solvents in two-stage liquefaction. As part of this project, the Xytel Corporation constructed a continuous reactor system to hydrogenate the solvents that will be used in this work.

The new project at Hydrocarbon Research, Inc., on a New Technology Concept for the Two-Stage Liquefaction of Coal is now in progress, and test results are just starting to come in. Preliminary data from microautoclave scoping studies and bench runs indicate that higher distillate yields were obtained at milder conditions than with existing single-stage technology. However, they have not yet achieved the predicted high level of distillate yields. Details of the initial work in all of these projects are included in the section "Project Management and Support/Liquefaction Industrial Technology Projects."

PROJECT MANAGEMENT AND SUPPORT

TECHNICAL SUPPORT OF MAJOR SYSTEMS' ACQUISITION

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

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 in various forms: (1) on-site technical support managers who are an integral part of the Oak Ridge Operations Office project team; (2) on-site technical managers at plant support facilities (PDU's and pilot plants); and (3) PETC-based technical support for the R&D support contracts.

H-Coal Pilot Plant Project

Ashland Synthetic Fuels, Inc.

All sections of the H-Coal Final Report have been completed by Ashland Synthetic Fuels, Inc. (ASFI), reviewed by DOE, and returned to ASFI for incorporation of DOE comments. With the exception of the Operations and Executive Summary sections, all DOE comments have been incorporated, and the sections reviewed and accepted by DOE; ASFI expects to assemble the entire document and submit it to DOE for final review by early February. A 2-3 week DOE turnaround is expected so that the report can go to publication sometime in March.

Hydrocarbon Research, Inc., is still reviewing the Piping and Instrumentation Diagrams for proprietary data. All non-proprietary P and ID's are to be included in the public version of the final report.

DOE/ORO and ASFI have negotiated an agreement to segregate, copy, and deliver the non-proprietary H-Coal technical files to the PETC Coal Liquefaction Data Base. The proposed cost is reduced by approximately 65K because ASFI is to perform the work without fee. It is also expected that the projected 12-month period to complete this task can be reduced to 6-7 months. Work has already begun, with staffing being implemented with the personnel retained to complete the Final Report.

Contractual actions are being taken to close out all inactive contracts. Sufficient obligated funds remain in the program to complete all foreseen work.

SRC Technical Data Analysis — Pittsburg and Midway Coal Mining Company

The report on Unit Operations Performance was completed and issued.

The report on process yields was completed and released. Yields were consistent among the three bubble column reactors with capacities of 50 pounds per day to 25 tons per day. Lower yields of distillate liquid were observed with CSTR reactors. Operation was stable over long periods of time with full product recycle.

The report on residence time distribution has been rewritten and submitted for approval. The following conclusions were reached:

- Bubble column tests highlighted the inaccuracy inherent in extending existing gas holdup correlations to different gas/liquid systems. Existing correlations for air-water systems appeared to be unable to consistently predict holdup for more complex systems.

- The P-99 reactor studies showed that increased dissolver height and gas velocities resulted in less efficient thermal backmixing.

- Radioactive tracer studies on the Fort Lewis reactor confirmed earlier hypotheses that the slurry phase was well backmixed, while the gas phase approached plug flow. The gas mean residence time and gas holdup were higher than predicted by bubble column correlations. Extrapolation of the resulting loss in slurry residence time to the Demonstration Plant operating conditions suggests that an increase in SRC yield of 5% mf coal beyond the design yield might have occurred at design operating conditions.

- Tests with a downcomer installed in the Fort Lewis reactor showed that it was a viable technique to recirculate slurry. Since the Fort Lewis reactor was already well backmixed, it was not possible to determine its effect on overall mixing; however, there was a slight shift toward isothermal conditions with the downcomer in service, indicating some improvement in mixing.

Physical, Chemical, and Thermodynamic Properties of Fossil Fuel Liquids

Work on physical properties measurements and coal-derived liquids characterization supported by this program is in progress at PETC, NIPER (National Institute for Petroleum and Energy Research, Bartlesville), and at five universities awarded grants during the last quarter. A recommendation for use of a PRDA as an appropriate vehicle for awarding new grants in the program for FY84 was approved at PETC and forwarded to Headquarters. A minimum of \$300,000 will be available under B&R AA 151510 to initiate support of new grants.

The PETC in-house characterization study has obtained fractions of H-Coal samples using each of two preparative-scale liquid chromatography separation schemes previously evaluated for coal liquids. A PETC team collected a well-documented set of samples from the most recent Wilsonville Pilot Plant run for future characterization studies.

Measurements of thermophysical properties of model compounds representative of fossil-fuel-derived liquids are continuing at NIPER. Studies are made on key compounds from pertinent chemical families to provide essential data for prediction of thermochemical properties of related compounds for which measurements have not been made, including the enthalpies of combustion, heat capacities, entropies and enthalpies along the saturation lines, vapor pressures, enthalpies of vaporization, vapor heat capacities, and spectroscopically derived thermodynamic functions.

The university grants cover work on properties measurements, correlation, and supercritical fluid characterization. Brown University has started viscosity measurements on pure compounds using oscillating disc and Cannon-Ubbelohde viscometers.

Purdue Research Foundation has studied desulfurization by stripping with supercritical steam for two coals and is constructing an apparatus for extraction of coal with organic solvents.

Rice University has completed design and ordered equipment for a constant pressure injection type apparatus to measure infinite dilution activity coefficients of discrete and narrow-boiling continuum mixtures.

Oklahoma State University has reactivated and tested a bubble point pressure apparatus for

determination of liquid and vapor phase compositions in equilibrium mixtures at elevated temperatures and pressures.

Brigham Young University is constructing a high temperature isoperibol flow calorimeter to study molecular interactions in coal liquids.

Wilsonville Process Development Unit

The PDU was down for planned maintenance and turnaround from September 26, 1983, to November 7, 1983. Run 245 began on November 7, 1983, and was continued throughout the quarter. The stated primary objective is to evaluate steady-state ITSL processing to produce high distillate yields feeding Illinois No. 6, Burning Star Mine coal. Hydrotreater catalyst is being added and withdrawn on a periodic basis in an effort to achieve and maintain a constant bed activity.

Several operating difficulties were encountered in November and December that may have delayed achievement of steady-state operation of the PDU. The difficulties encountered were believed due in part to poor weather conditions. On December 25, 1983, the PDU was forced down due to apparent inability to maintain operating temperatures under near zero degree weather conditions. The PDU remained down for the remainder of December.

FIRST STAGE OPERATIONS

For Run 245, the dissolver is set at 1/4 capacity, and the temperature maintained at 810°F. Coal feed rate is somewhat reduced to accommodate a lower space rate in the hydrotreater. Operation of the Thermal Liquefaction Unit (TLU) was reasonably smooth until late November, when problems were encountered with the vacuum tower pumps and heater.

Shortly thereafter, the TLU was upset due to a severe rainstorm. In early December, the slurry preheater failed several times. A steam boiler also failed during this period, causing unsteady vacuum tower pressure.

KERR-McGEE CSD UNIT OPERATIONS

The CSD unit operated relatively well during this period considering the problems experienced with the TLU. Resid recovery has ranged from 89% to 93%, and energy rejection has varied from 20% to 24%. Some incidence of ash concentrate extrudation was reported.

H-OIL HYDROTREATER OPERATIONS

In early November, the ebullating feed pump control valve failed, causing the bed to slump. Periodic catalyst addition/withdrawal was initiated at the end of November, with the bed temperature maintained at 720°F and space velocity maintained at 0.75. The catalyst addition rate used is equivalent to one pound of fresh catalyst per ton of coal fed. In early December, hydrotreater makeup compressor problems caused a temporary shutdown. Ebullating pump seal flush differential pressure fluctuations continued through mid-December. This problem, as observed in the past, preceded eventual pump failure.

FUTURE WORK

Operations with a western bituminous coal are planned for early 1984. An ITSL run with deashing after hydrotreatment is also planned for next quarter.

PROJECT STATUS

Negotiations for an eleven-month extension of the existing contract are expected to begin in late-January 1984. Operations under the new extension would be extended to December 31, 1984.

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.

Coating Studies for Coal Conversion — Oak Ridge National Laboratory

The objective of this task is to develop titanium diboride (TiB₂) coatings that offer the hope of extending the life of valve trim material in coal conversion applications. The scope of the task is limited and consists of using available equipment to deposit TiB₂ coatings onto cemented carbide and nickel-bonded TiB₂ substrate disks. The erosion rate of such coatings will be determined using an established test in order to evaluate whether TiB₂ coatings appear promising for valve trim and other severe erosion environment fossil applications.

Previous erosion testing of ORNL Chemical Vapor Deposition coatings of TiB₂ showed such little wear that the erosion crater depth was difficult to determine from the variation of the surface finish of the as-deposited coating. During this period, coatings were deposited under conditions designed to produce a smoother surface. Although the coatings were smoother visually and to the touch, the profilometer data indicated that the surface variations are still in the range of a few micrometers. Erosion testing at Battelle Columbus again showed a high resistance to wear, with a crater depth of 0 to 2 μm, essentially within the variation of the as-deposited coatings. Previous characterization had shown that coatings deposited at 800°C were not nearly as hard as coatings deposited at 900°C. Additional coatings deposited from 900°C to 1000°C showed some increase in hardness as the temperature increased. All the coatings in the 900°C to 1000°C range were very hard (32 to 44 GPa Knoop microhardness for a 50-g indenter load), but the 900°C coatings are preferred because they are smoother.

Another significant coating property that varies with deposition temperature is the chlorine content. Although actual concentrations were not obtained, the chlorine-to-titanium intensity ratios for coatings deposited at 800°C, 900°C, and 1000°C were 0.187, 0.021, and 0.008, respectively. Whether or not the chlorine content significantly affects the erosion performance has not yet been determined.

Coal Liquefaction Pilot Plant Materials Testing and Failure Analysis — Oak Ridge National Laboratory

The objective of this project is to investigate the causes of materials degradation in the Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Ala. The work to be performed includes the exposure and analysis of corrosion coupons and U-bend specimens, the analysis of failed components from various process areas of the plant, chemical analysis of selected process streams, and on-site examination of components.

As a result of previously funded activities, ORNL has established a materials testing and failure analysis program at the Wilsonville Advanced Coal Liquefaction Facility. Currently, ORNL has 26 corrosion coupon and U-bend specimen racks in place at Wilsonville. The corrosion coupons provide for testing of a range of alloys for resistance to corrosion. The U-bend specimens are stressed alloys that are exposed in

process streams that have the potential to cause stress-induced corrosion of structural materials.

During this quarter (October 10-11), a trip was made to the Wilsonville facility during their scheduled fall shutdown. During this visit, a Krautkramer-Branson ultrasonic thickness gage was used to measure the thickness of vessel walls, heat exchanger tubes, and transfer lines; and corrosion samples were examined or replaced so that corrosion rates could be calculated. The insides of several of the vessels were also examined.

The ultrasonic inspections showed an appreciable thickness change for only one set of heat exchanger tubes. All measurements were recorded for reference when the next series of thickness checks is made.

Ten racks of corrosion samples were evaluated during this trip. Samples from two racks were cleaned, weighed, and reinstalled. The samples from six other racks were replaced, and the exposed samples returned to Oak Ridge for examination. Two other racks were replaced with a different type of rack. Both the coupons and U-bends exposed in the V-103 high pressure separator suffered severe corrosion of the alloys that contained less than 11% chromium. These data confirm other observations that a stainless steel liner is needed for a vessel operating at the V-103 conditions [$>315^{\circ}\text{C}$ ($>600^{\circ}\text{F}$) and 13.8 MPa (2000 psi)]. Low corrosion rates reflect the relatively innocuous conditions of the V-105 solvent decanter, which operates at about the same temperature as V-103 but at a much lower pressure. Corrosion rates in V-110 are similar to, but somewhat less than, those in V-103. Corrosion rates for alloys exposed in two tanks, V-164 and V-170, that operate near ambient temperature were very low. Coupons exposed in vessel V-502, a flash drum in the Kerr-McGee area, showed low corrosion rates. Coupons exposed above tray 1 of the vacuum column at about 95°C (200°F) had low corrosion rates. Samples exposed below tray 8 at about 205°C (400°F) showed that corrosion was greater in the lower portion of the vacuum column. The samples exposed in the hydrogenation reactor were subjected to pressures and temperatures at least as high as those in the R-101 dissolver. The carbon steel and Inconel 600 experienced appreciable corrosion, but the corrosion rates of the other alloys were fairly low.

A metallographic examination of nine of the austenitic alloy U-bend specimens exposed in V-103 or V-110 did not reveal any evidence of stress corrosion cracking.

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 plunger pumps currently used in the pumping of hot, erosive coal particle slurries in coal-derived oils. The improvement will be directed towards eliminating or solving the packing and plunger maintenance problems in the stuffing box. The effort involves the development of two separate sealing concepts (using a clear oil buffer system in each system) that isolate the stuffing box from the hot, erosive slurry. In each concept, the buffer fluid will serve as a driver to pump an equal volume of slurry situated on the opposite side of the seal.

Ingersoll-Rand Research, Inc., has tested three of the floating piston type seals in a slurry environment by using a seal evaluator device. The seal evaluator operated the seals at design speed and stroke with a 40% sand slurry on the appropriate side of the seal and with a clear buffer liquid on the other side.

All three seals have maintained a solids contamination level in the clean buffer liquid of no more than a few hundredths of a percent. This level of sealing was held constant through the 200-hour wear tests. The projected life of the seals is 350 to 600 hours in sand. The equivalent life in coal is conservatively estimated to be 3500 to 6000 hours. The program life goals appear attainable with these new type seals.

The diaphragm seal has been 90% machined. The reciprocating pump has been tested with water at the Ingersoll-Rand Standard Pump Division. The pump is to be delivered to the Ingersoll-Rand Research Center on January 1, 1984.

Scoping Study of Technology Needs for Coal Liquefaction Critical Components — Oak Ridge National Laboratory

The purpose of this task is to identify scale-up-related technology gaps in coal liquefaction slurry pumps and slurry letdown valves. An assessment of the scale-up factors anticipated for commercial plants, the data gaps, and the development needs will be made for these two components.

During this reporting period, the drafts of the topical report on both the slurry pumps and the valves were transmitted to PETC. Activities in this project have been terminated.

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:

In the hydraulic studies, Ingersoll-Rand continued the screening and evaluation of design features and improvements with a 4-inch impeller on a small-scale tester operating at 6000 rpm. This testing was carried out with water, water/sand, water/sand/viscosity additive, with the viscosity varying from 1 to 300 centistokes at shear rates of 1000 to 2000 sec⁻¹. The following six basic tests were performed during this quarter:

- SST 5004 - Evaluate radiusing of the volute cutwater; study wear at various locations.
- SST 3005 - Preliminary performance evaluation with high viscous slurry; study wear with high viscous slurry; and provide loop operational experience with high viscous slurry.
- SST 5006 vs. 5007 - Comparative test evaluation of following design features: (1) MK II side-walls and volute; (2) pump-out vanes; (3) concave cutwater radius trim; and (4) directed leakage path.
- SST 3008 vs. 3009 - Comparative test evaluation of following design features in traditional slurry pump: (1) number of vanes (4 vs. 5); (2) directed leakage path; and (3) thick concave radius cutwater.

- SST 5010 vs. 3011 - Study the wear on pump internal components of low blade loading and traditional design approach.

- SST 3012 and 3013 - Comparative test evaluation of following design features with viscous slurry (80 centistroke at 100 sec⁻¹): (1) circular collector; (2) impeller square vs. round edge; (3) thick concave radius cutwater; and (4) directed leakage path design concepts.

The performances with respect to head vs. flow characteristic, power consumption, and efficiency were compared for the above configurations. The drop in performance due to slurry concentration was also established. Furthermore, the wear location, type of wear, and the cause of wear were studied during each test, with the objective of understanding and minimizing the wear in the slurry pump. All the information obtained during the testing is being evaluated and analyzed in order that the prototype pump hydraulics can be designed with features that have shown promise during the testing.

In material studies, the results obtained from the three laboratories (ORNL, Battelle, and Ingersoll-Rand Research, Inc.) were interpreted and analyzed during the quarter.

The ORNL corrosion tests indicated that both currently used materials (HC 250 and 1503) have very low corrosion rates, less than 1 mil per year.

The comparison of material ranking obtained with erosion tests at Ingersoll-Rand (sand/water and viscous sand/water/viscosity additive) and Battelle (hot coal-oil) is shown in Table 1. For sand/water tests, there is a direct correlation between the hardness of the materials and their erosion resistance; a quantitative correlation be-

**Table 1.
Ranking of Materials**

I-R Sand-Water	I-R Viscous Sand-Water	Battelle T-102
1) Boronized HC 250	1) Boronized HC 250	1) SIC
2) Eutectic 6715	2) SIC	2) Eutectic 6715
3) SIC	3) Eutectic 6715	3) HC 250 (FH)
4) 1503	4) HC 250 (FH)	4) Boronized HC 250
5) HC 250 (SA)	5) 1503	5) 1503
6) HC 250 (SA)	6) HC 250 (SA)	6) HC 250 (SA)
7) HC 250 (FA)	7) HC 250 (FA)	

FH = Fully Hardened
FA = Fully Annealed

SA = Semi-Annealed
1503 = White Cast Iron

tween the hardness and wear resistance could not be established. Viscous sand/water test results also show the same correlation except for the 1503 material. However, the hot coal-oil results do not show any such correlation.

In any slurry erosion test, the erosion rate does not remain constant; the rate decreases in the beginning and then tends to stabilize after a period of time. This "saturation effect" is important when a very small material thickness is removed from the specimen during the test. In the hot coal-oil test, the thickness removed was very small, considerably smaller than in sand/water tests. It is not known how much effect this "initial erosion rate" had on the "overall erosion rate," since the erosion depth was not determined as a function of time.

During the quarter, the new alloy development work was also carried out in the Ingersoll-Rand laboratory. Two basic approaches were considered; (1) higher chrome (more than 30%) iron and (2) high phosphorous-high chrome iron.

The second approach offers more promise and therefore was pursued initially. The castings from this alloy were analyzed for microstructure and hardness. Erosion tests were performed in the nozzle tester using viscous sand/water slurry. The work to date is encouraging, and it indicates that developing a new alloy is technically feasible. However, considerable work is required before commercially acceptable alloys can be developed.

The analysis of all the test results to date indicates that the boronized HC 250 and Eutectic 6715 materials offer most promise for coal liquefaction centrifugal slurry pumps.

The development of a prototype pump test facility is progressing well at Ingersoll-Rand. This facility will permit testing of two pumps simultaneously on a continuous basis with sand/water slurry for flow up to 300 gpm and head up to 300 ft.

The test bed frame for a 200-hp motor, two pumps, and belt drive system was fabricated and installed in the laboratory. The major components, such as slurry booster pump, slurry mixing tank, water tank, heat exchanger, radiator, cyclone, and sand silo, have been procured and installed. The piping and electrical installation work has been initiated, with anticipation of completion during early 1984.

The prototype pump specification was established, and preliminary design and selection of components, such as bearings, shaft, lubrication, frame, and seal, have been started. Ingersoll-

Rand will supply two prototype pumps with motor, drive, etc., mounted on bed plate. The general arrangement drawing is also being prepared.

Coal Slurry Loop: Conceptual Design — Argonne National Laboratory

The objective is to conceive, design, and cost a coal slurry test loop suitable to test research equipment that is being built.

Argonne National Laboratory has completed the conceptual design of the coal slurry loop and has also completed the economic analysis of constructing and operating the test loop. The results were presented to PETC and HQ in October. Following the presentation, DOE considered that the cost exceeded the planned anticipated cost and has decided to terminate the project and search for much less costly and less complicated ways to test equipment that is being built.

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 observation points.

In this quarter, emphasis of the program was on assessing the accuracy of the cross-correlation technique in slurry velocity measurement, both experimentally and theoretically. Argonne National Laboratory (ANL) carried out a series of coal-water slurry flow tests at the solid-liquid flow tests facility. Using Ohio No. 9 coal of various slurry concentrations of 22 wt%, 34 wt%, and 39 wt%, they tested at velocities of 1 to 4 m/s in a 2-inch pipe.

The transducer arrangement and associated electronics were designed. The transducers were clamped directly on the pipe located at a test station of the loop. Their spacing and orientation were adjustable, which allowed the effect due to sensing geometry to be evaluated. The setup of electronics was similar to that in previous work but with two slight modifications: (1) the use of a frequency synthesizer that can provide a steady driving signal at any frequency, selectable digital-

ly, and (2) the arrangement of phase shifters and mixers; the phase shifters were placed between the received signals and the mixers, which allowed us to adjust the desired phase angle between received signal and driving signal so that maximum output with proper phase can be obtained.

The phase-shifter adjustment was more important for the coal-water slurry than for the coal-oil case, because smaller modulation was detected from the coal-water slurry flow.

The choice of operating frequency has two prime criteria: (1) the direct acoustic transmission through the pipe wall must be minimal, and (2) the acoustic wavelength in slurry must be compatible with the size of flow modulation, such as particle or cluster size.

Within the frequency range of the transducer used for the test, 824 kHz and 1.95 MHz were the frequencies that provide optimum signal strength across the slurry in a 2-inch pipe. Between the two frequencies whose wavelengths in the slurry are 1.8 mm and 1 mm, respectively, the 1.59 MHz frequency induces a signal modulation about four times that by 824 kHz. However, the shape of the correlation function and its peak position are not affected by the difference in operating frequency. The increase in magnitude of the correlation function by using 1.59 MHz indicates that the size of a cluster, if it exists, may be close to or >1 mm, corresponding to roughly ten times the particle diameter (average particle diameter = 100μ).

Both horizontal and vertical transducer orientations were employed during the tests. No significant change in measured cross-correlation functions was detected; even at 39 wt% coal, settling was not observed. The use of three pairs of transducers allowed ANL to obtain cross-correlation functions at three transducer spacings simultaneously. The measurement was made during a run at 22 wt% slurry concentration and 3.09 m/s average slurry velocity. Under these conditions, the flow was in the turbulent regime. A slight asymmetry developed when the spacing was increased. Little difference between the peak and the centroid of the correlation function can be found. The peak times for the three spacings are consistent within 2%, which is partially due to the error in spacing measurement.

Air-bubble injections into the slurry were carried out during some of the tests to evaluate the effect on cross-correlation due to the presence of bubbles in the slurry. The cross-correlation function was distinctly different when bubbles were introduced. Large bubbles, about the order of the

acoustic beam width, affect the modulation because of the difference in impedance. Smaller bubbles tend to produce a complex correlation function with multiple peaks. The effect of bubbles is not well understood now, and further tests are needed to establish a relationship.

The velocities measured by cross-correlation techniques were compared with those obtained by a flow diversion method, and most values fall within 5%. (The flow diversion method is also accurate within 5%.) This indicates that a constant meter factor of about 0.85 is needed to bring the correlation velocity to the average pipe velocity.

Work is being continued on the evaluation of the velocity profile effect on the cross-correlation function. The design of an integrated electronic package has been initiated.

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 (1) reciprocal and (2) centrifugal slurry pumps suitable for (a) coal liquefaction plant service and (b) conceptual scale-up to demonstration and commercial size in a feasible and economical form.

The seal hardware fabrication is in progress. The reciprocating seal rings and O-rings have been received. The purchase orders for both the centrifugal and reciprocating pumps have been issued, and the scheduled delivery dates are mid-January and early March, respectively. The reciprocating pump tester design was revised to make the suction and discharge flush fluid plungers larger and of the same size to simplify fabrication. The extra flush fluid flow will provide additional design margin and can be bypassed to regulate the required flow.

The task 3B Laboratory Test Plan was completed and approved by PETC and released to several facilities for quotation buildup and testing. Several quotations were received and evaluated. Wyle Laboratories-Norco was selected. Release of purchase order is pending PETC approval. Preliminary facility design has been started to ensure meeting the required completion date.

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.

The Phase I topical report has been completed and submitted to PETC. The assessment of Phase I by SAI is that useful accuracy has been demonstrated for an installation of a Dual Energy Gamma Gage at the preheater exit. If a slag flow regime is found, then only the gas phase density data are required because input solid and liquid phase density can be derived from the gage. Alternatively, if phase densities are known, then ash concentration can be determined. In dispersed flow, liquid and solid phase densities are required. The Phase II approval has been issued to SAI to begin the design and fabrication of the meter.

Development and Evaluation 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 are directed at each other

in order to dissipate the resulting high rubbing energy and pressure-collapsing energy.

Pacific Valve was contracted in this quarter to initiate the development of the valve. Because of the unavailability of larger test loops, Pacific Valve has been directed to design a valve suitable for testing at Wilsonville.

Micro Motion Flowmeter Evaluation — Mound Laboratory

The objective is to develop a high temperature flowmeter for the viscous slurry line.

Micro Motion, Inc., of Boulder, Colo., was sub-contracted to develop a flowmeter rated for 3300 psig and 900°F. In the development of the flowmeter, several tests were investigated to ensure that the flowmeter will perform to design conditions. In the previous quarter, the prototype was installed and tested on the Wilsonville CSD feed line, and several calibrations were needed to provide an acceptable precision. During the past quarter, both the high temperature flowmeter and another unit designed for low temperature services have been operating fairly well. These meters have been turned over to the operating contractor for routine operations.

LIQUEFACTION INDUSTRIAL TECHNOLOGY PROJECTS

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

The overall objective of this activity is to develop, implement, and manage coal liquefaction industrial research and development projects for expanded use of coal as a petroleum substitute.

Indirect Liquefaction

The 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.

Phase I and Phase II tasks continued to be the focal point of the program for this quarter. Specific tasks included Task 2 - Engineering and Design Specification; Task 3 - Procurement; Task

5 - LaPorte LPMeOH PDU Renovation, Installation, and Shakedown; Task 7 - Laboratory Support Program; and Task 11 - Project Evaluation and Reporting. Activities associated with each task were the following:

Task 2 - Engineering and Design Specifications

- The award of a painting and insulation subcontract for the LaPorte Liquid Phase Methanol (LPMeOH) PDU.
- The finalized submission of the LaPorte LPMeOH PDU Operations and Maintenance Manual.
- The preparation and submission of the contractually required finalized LaPorte LPMeOH PDU Deactivation Plan and associated procedures. Implementation of the Deactivation Plan and Procedures will occur at contract completion.
- The design and assembly of the main control panel for the LaPorte LPMeOH PDU.

Task 3 - Procurement

- Completion of required Quality Assurance Source Inspections for all new equipment purchases for the LPM₂OH PDU, and shipment of the equipment to the LaPorte, Texas, project site.

- Procurement of spare parts to support the planned operation of the LaPorte LPM₂OH PDU is continuing.

Task 5 - LaPorte LPM₂OH PDU Renovation, Installation, and Shakedown

- Mechanical equipment and aboveground piping installations are now complete.

- Electrical and instrumentation installations are now complete.

- Insulation and painting are 95% complete.

- Shakedown and startup procedures for the LaPorte LPM₂OH PDU were developed.

- A hydro-flush of the LPM₂OH using cold, demineralized, low-chloride water was completed.

- A pneumatic pressure test of the LaPorte LPM₂OH PDU using nitrogen gas was completed.

- Calibration of instrumentation and the reactor's nuclear level detector is now in progress.

- Installation of the DEC analytical/data acquisition system is nearing completion.

- The computer hardware consists of a Digital VT103 microcomputer (a PDP-11/23 microprocessor inside a VT100 video terminal) with 128K words of memory. A proprietary AIM/ACP software package will be utilized for computer control. This version is a disk-based system that utilizes a fixed disk unit with a floppy disk backup. Additional hardware includes a DEC LA120 hard-copy terminal (printer plus a keyboard), a VT100 video terminal (in the control room), a VADIC 1200 baud modem, and CPI interfacing gear. The modem will allow for dial-in capability from Allentown (Air Products and Chemicals, Inc.), Fairfield (Chem Systems, Inc.) and Tarrytown (Chem Systems, Inc.) to obtain reports without interfering with the data acquisition functions of the system.

- For the analytical portion of the system, gas analysis will be performed using two on-line gas chromatographs (Carle Instruments). The gas sampling system, which includes a multistream sample rotameter panel and automatic stream selector station, is provided with timers and automatic switches so that these analyses can

proceed virtually unattended. Liquid samples of oil and product methanol will be analyzed using two liquid sample chromatographs (Schimadzu Scientific Instruments). A Spectra-Physics 4000 electronic integrator with three DIM (Data Interface Modules) is also provided to interface the chromatographic analyses with the microcomputer. An Epson MX-80 hardcopy printer is provided for recording GC analyses. In addition, each DIM on the Spectra Physics 4000 has a separate strip chart recorder for GC analyses. Finally, a Karl Fischer apparatus and an analytical balance are available for water determination and sample weighing.

- The software development, using DEC/AIM data base structure, has covered the definition of all variables, mathematical manipulations, frequency of signal scanning, use of units, and correction factors. Provisions for on-line status displays were made, and the formats of hourly and daily hard copy reports were discussed and partially put in final form.

- Training sessions were completed for APCI personnel who will supervise and operate the LaPorte LPM₂OH PDU.

- The LaPorte LPM₂OH PDU Operations and Maintenance Manual was put in final form.

- A two-day Operational Readiness Inspection (ORI) was conducted to review the LPM₂OH PDU unit. Representatives from DOE and APCI's Safety, Operations, Start-Up, Project, Process, and Construction groups participated.

- A punch list of changes, deficiencies, and required corrective actions was developed.

- Work is in progress to resolve ORI punch list items.

- Preparations are now being made for hydrotesting with demineralized, low-chloride water. Following a successful hydrotest, run-in of the reactor slurry loop system with cold and then hot demineralized water is planned. This will be followed by run-in of the system with cold and then hot Freezene 100 mineral oil. These system tests will be then followed by two-phase gas holdup studies.

- A two-phase gas holdup test plan for the LaPorte LPM₂OH PDU has been developed. Studies called for by this plan will permit the correlation of APCI computerized models and mathematical correlations based on stirred autoclave and Fairfield LPM₂OH Lab PDU gas holdup data.

Task 7 - Laboratory Support Program at Air Products Chemicals, Inc. (APCI)

- In the APCI 1-liter stirred autoclave reactor, catalyst F50/4E75-81 (ICI commercial powdered catalyst) was tested in base-line activity runs with balanced gas at 225°C and 250°C, 500 and 900 psig, and 5000 and 10,000 L/hr-kg space velocity. Data from these experiments were used for comparison with CSI Fairfield Lab PDU results and in the fundamental modeling effort.

- Analyses of Freezeze 100 oil samples from autoclave runs were conducted to characterize the stability of the oil under reaction conditions. These analyses showed a shift in the oil molecular weight distribution to higher-chain hydrocarbons, suggesting some loss of lighter components, but no evidence of cracking or polymerization was found.

- Mass transfer effects in the autoclave were studied using a classical stirrer speed experiment. Methanol productivity and CO conversion were measured using balanced gas at 250°C and 270°C, GHSV of 10,000 and 12,000 1/hr-kg, and 885 psia. The autoclave stirrer speed was varied from 800 to 2000 rpm. No significant change in productivity was seen with stirrer speed, suggesting little significant mass transfer control in the autoclave.

- The gas phase screening program of up to 25 new exploratory slurry catalysts was completed. From the overall effort, three candidates were chosen to progress to liquid phase testing in the CSI Fairfield 2-liter autoclaves. Five samples of three new exploratory catalysts were prepared and delivered to Chem Systems for testing in the slurry phase. These five samples consisted of one Raney copper type catalyst, two preparations of the copper/zinc/alumina catalyst derived from the Stiles patent, and two preparations of a copper/zinc/boron catalyst.

- A draft of the Topical Report detailing the liquid-entrained experimental catalyst preparation and testing program has been completed.

- An analysis of the method used to calculate gas holdup from CSI's February/March, 1982, ebullated Lab PDU experimental data was conducted to understand the sensitivity of calculated gas holdup to variations in experimental measurements. Analysis shows that the calculated ϵ_G is very sensitive to changes in three-phase bed density and catalyst particle density used in the calculations. The analysis also shows that catalyst loss via carryover or attrition during operation must be accounted for in calculating

gas holdup via this method. Several methods for measuring gas holdup in the Fairfield and LaPorte PDU reactors were examined, and recommendations made for the best methods considering accuracy and operating constraints. A direct bed density (nuclear) method used at Fairfield and planned for LaPorte was confirmed as the best measurement method. Gas holdup is calculated from measured catalyst bed densities for liquid-only and gas-liquid flow conditions. The method is insensitive to coupled errors in measured densities.

- Gas holdup in an ebullated-bed bubble column was measured during the recently completed HRI cold flow reactor tests on ebullated catalyst EPJ 19H. Tests were run with an N₂-heptane system on both oxide and reduced catalyst. Gas holdup varied with gas velocity from 10.5% to 24.5% over a superficial gas velocity range of 3.9 to 9.1 cm/sec. Comparison of data for oxide and reduced catalyst showed little difference between measured ϵ_G . The gas holdup data were compared with ϵ_G values from established literature correlations for gas-liquid and gas-liquid-solid systems. Measured gas holdup falls in the middle of the ϵ_G range predicted by the two-phase correlations; the three-phase correlations underestimate measured ϵ_G .

- Viscosity measurements of 20-wt% and 30-wt% catalyst slurries in Freezeze-100 oil were completed. The catalyst used for the measurements was powdered F50/4E75-83 (ICI). In general, the catalyst slurries behave as non-Newtonian fluids. The slurry viscosity was dependent on shear rate, as well as on temperature and catalyst loading. The highest viscosities, 150-250 cp, occur for the 30-wt% slurry at low temperature and shear rate. Previous estimates based on general correlations underestimated the LPMeOH slurry viscosity by as much as 500% to 700% at low shear rates.

- Analyses of crude methanol produced in the Fairfield LPMeOH Lab PDU during ebullated-run EPJ 19LR (July/August, 1983) were made to assess product purity and other property information. Methanol from both balanced and CO-rich gas feeds were characterized.

Task 7 - Laboratory Support at Chem Systems, Inc. (CSI)

- The first liquid-entrained run in the Fairfield, New Jersey, LPMeOH Lab PDU was completed. Using ICI powdered methanol catalyst F50/4E75-01 and a catalyst loading of 17 wt%, an

87-hour run on both balanced and unbalanced synthesis feed gases over 12 process variable conditions was completed. The catalyst was reduced in situ. Carbon monoxide conversion levels, methanol productivities, and gasholds for the balanced synthesis gas were comparable to those observed in the autoclave for balanced gas. With unbalanced gas, conversions and productivities were slightly lower in the LPM₂OH Lab PDU.

- A long-term activity maintenance run on ICI powdered methanol catalyst F50/4E75-01 at 5,300 kPa, 250°C, and 5,000 L/hr-kg catalyst was successfully completed in a 2-L autoclave:

- This test involved operating at conditions identical to those selected for the LaPorte batch check of R71/OF12-26 in the Lab PDU conducted in July-August, 1983. The autoclave test lasted 2,267 hours and accumulated a methanol productivity of 792 kg/kg catalyst. The CO conversion decreased from 13% at the beginning to 8% at the end of the run. Methanol productivity decreased from 15 gmol/hr-kg catalyst initially to 8 gmol/hr-kg catalyst. This rate of catalyst deactivation is comparable to that achieved with balanced gas in the vapor phase and is considered an interesting result for the CO-rich synthesis gas case.

- In addition, this run demonstrated that procedures employed for the detection and prevention of poisons such as chlorine and iron carbonyl from reaching the catalyst bed were totally effective. As was evident from the data, weekly change-out of activated-carbon guard beds prevented virtually all poisons from contaminating the methanol synthesis catalyst. This may explain why activity maintenance was better than expected based on historical evidence with CO-rich gas.

- A 510-hour run on liquid fluidized catalyst EPJ-25L, R71/OF12-25, was completed. The primary purpose of this run was to obtain a comparison of the R71/OF12-25 batch and the R71/OF12-26 (EPJ-19LR) batch in order to determine which catalyst to use at LaPorte. Preliminary results indicated that the R71/OF12-25 catalyst is less attrition-resistant than the R71/OF12-26 catalyst tested in July-August. Also, its methanol synthesis activity seems to be slightly lower. Chem Systems has, therefore, recommended catalyst R71/OF12-26 for liquid-fluidized operations at LaPorte.

Task 11 - Project Evaluation and Reporting

- Monthly Progress Status Report, monthly cost reports, and quarterly Technical Reports were prepared and issued.

- Information from the APCI and CSI autoclaves, and the LPM₂OH Lab PDU (Fairfield, New Jersey) continued to be evaluated. Data are being assimilated into the fundamental modeling effort to allow better predictions of rate constants, particularly for the CO-rich unbalanced synthesis feed gas.

Results of model predictions versus real data obtained from the autoclave and LPM₂OH Lab PDU have been correlated.

In the next quarter, work will continue on Tasks 5, 7, and 11. Task 2 and Task 3 work will be complete. Work on Task 6 — Liquid-Fluidized Operation in the LaPorte, Texas, Liquid Phase Methanol (LPM₂OH) PDU — will be initiated. Topical reports summarizing the liquid-entrained experimental catalyst development program, and liquid-entrained/liquid-fluidized runs in the Fairfield LPM₂OH Lab PDU will be issued.

Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels — Mobil R&D Corporation

The objectives of this work are to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H₂/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 and 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.

The design phase of modifications for the two-stage unit (CT-256) is completed. The construction phase of the modifications will begin soon.

A particle-size analyzer, "Sedigraph 5000E" by Micromeritics, Inc., is being evaluated for measuring F-T catalyst particle-size distribution. Two standard samples of sizes 0.35 to 35 μm and 1 to 20 μm were submitted for analysis, and good agreement was obtained in both cases. Analysis of the fresh catalyst I-B gave a median (50 wt%) particle size of about 4 μm.

The on-site and off-site construction of the tall hot-flow nonreacting columns is in progress and on schedule. Scoping hydrodynamic studies using a reactor-wax sample from Run CT-256-5 in a 5.3-cm-i.d. x 2.1-m-high hot-flow column were conducted. At superficial gas velocities up to 3.5 cm/s, the gas holdups were less than 12 vol%, substantially less than what was observed using a reactor-wax sample from Run CT-256-3 and that predicted by Deckwer's correlation, i.e., $\epsilon_G = 0.053\mu^{1.1}$. This indicates that different Fischer-Tropsch reactor waxes may give rise to different gas holdups.

Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process — Air Products and Chemicals, Inc.

Slurry Reactor Design Studies

Gas Holdups

In general, gas holdups have been lower in the 12-inch column than in the 5-inch column. A test with paraffin in the 12-inch column at two different bed heights, 5 ft and 15 ft, showed no difference in the average gas holdup. Therefore, bubble coalescence due to increasing column height is not a factor in the smaller gas holdup observed in the 12-inch column.

Heat transfer coefficients were measured in the two-phase paraffin/N₂ system. As with the three-phase slurries, the results were lower than predicted by Deckwer's correlation (around 36% less).

Bubble Diameter Measurements

The double conical probe was inserted into the 12-inch column to collect initial data using a 0.5-5 μ m Fe₂O₃/paraffin slurry. A typical bubble trace response showed the change in thermal conductivity detected as the bubble passed first the lower, then the upper probe. A derivative was used to determine the beginning and end of the bubble pulses, from which dwell times and lag times were calculated. Using criteria that allow for the nonrigidity of the bubbles, the data acquisition system accepts about 1 in 9 bubble traces, analyzed at the rate of approximately 1 per second. In order to obtain 10% accuracy in the mean bubble diameter, 1,400 chord length samples are required, equivalent to about 4 hrs of run time.

The range of bubble chord lengths determined in this first test of the system extended from 0.02 to 2.3 cm, with 98.6% less than the 1 cm. A gamma distribution function is fitted to the bubble

chord lengths as the initial step to determining the Sauter mean bubble diameter.

Slurry Viscosity

Slurry viscosity can affect gas holdup, bubble diameter, and, to a lesser extent, heat transfer. As the solid loading in the slurry is increased, viscosity effects can become noticeable. To try to account for the effect of viscosity in correlating the bubble column hydrodynamics, viscosity measurements were carried out (by Tekmar) on some representative slurries used in the cold flow modeling, i.e., 30-wt% slurries of 1 to 5 μ m Fe₂O₃, 90 to 106 μ m Fe₂O₃, and 90 to 115 μ m SiO₂ in paraffin. Identical values of shear stress versus shear rate measurements observed with the large particle size Fe₂O₃ and SiO₂ were not expected, and the measurements will be repeated. The slurry viscosity data for Fe₂O₃/paraffin slurries were correlated as a function of shear rate to the power of 0.502 and 0.533 for the small and large particles, respectively.

To apply this data, an estimate of the shear rate in a three-phase bubble column is necessary. Nishikawa, Kato, and Hashimoto determined bubble column shear rates in two-phase Newtonian and non-Newtonian systems by measuring deviations from theoretical heat transfer coefficients. The shear rates they calculated were proportional to the square root of the superficial gas velocity in the column. Using their correlations, shear rates of 173 to 762 sec⁻¹ were predicted over the range of linear gas velocities used in the cold flow model columns. The slurry viscosities, therefore, are estimated to vary by a factor of approximately two over the range of parameters studied in the cold flow modeling experiments. This approach will be used in attempting to correlate further the effect of slurry viscosity.

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 and a shape-selective molecular sieve component to control hydrocarbon boiling range and quality.

In a patented procedure, modifications to Union Carbide's Zeolite Y had earlier been shown to result in a hydrophobic form of the zeolite, known

as UCC-101. While Zeolite Y itself, with a larger pore opening than Mobil's ZSM-5, has weak activity for methanol or propylene conversion, the hydrophobic form of Y, namely, UCC-101, provided significant conversion to a hydrocarbon product containing both gasoline- and diesel-range fractions. This development by Union Carbide investigators is of considerable interest from the viewpoint of inducing catalytic activity into molecular sieves of various pore sizes, which then may catalyze the synthesis of different hydrocarbon product ranges.

A catalyst consisting of cobalt and UCC-101 was effective in the conversion of synthesis gas to a hydrocarbon product, of which 70% was observed to boil in the motor fuel range, i.e., C₅-700°F. The product contained 14.5% methane; and 5.3% of the product boiled above 700°F. A hypothetical catalyst having an exact Schulz-Flory product distribution could at best produce 72% of the product in the motor fuel range. Such a hypothetical catalyst would produce less than 3% methane and almost 9% of hydrocarbon material boiling above 700°F. It is interesting that the Union Carbide catalyst provides a motor fuel fraction approaching the theoretical limit despite the fact that the methane yield is quite high. It is possible that a separate methanation mechanism is operative and, if suppressed by suitable catalyst modification, might further enhance the motor fuel yield. Recent efforts have reduced the methane yield by 30%. Further research in this direction is currently in progress.

Two-Stage Liquefaction

The goal of this technological area is to 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.

Integrated Two-Stage Liquefaction PDU — Lummus

Subtask 1.1, integrated operation with Wyodak subbituminous coal, was completed. Operations were satisfactory because of unexpectedly high-quality solvent. A new SCT reactor was fabricated, installed, and operated as part of the modified Subtask 1.2 program. Subtask 2.2 resumed and was completed. The results indicate that rehydrogenation of the recycle solvent occurs rapidly and with excellent hydrogen efficiency. Conversion of extract to distillates requires

longer residence time and more severe reaction conditions. Construction of the bench deasher for Task 4 was completed.

Subtask 1.1 - Integrated Two-Stage Liquefaction of a Sub-bituminous Coal SCT

Conversion of Wyodak coal to quinoline solubles remained at 86% to 90% to the end of Subtask 1.1. An increase in throughput, to eight gallons per hour, equivalent to seven minutes in the soaker at 840°F, had no effect on conversion. This indicates that dissolution is faster than expected, and longer residence times may result in retrogressive reactions. Molecular hydrogen consumption remains at zero, while hydrogen transfer from the solvent is 1.5% to 2.0% of coal, which is more than was transferred to Illinois bituminous coal. The lighter product distribution has, therefore, required more hydrogen, which is being satisfied entirely by the solvent. About 45% of the recycled extract in the deasher underflow is converting to quinoline solubles.

A new plug-flow reactor was installed to replace the soaker. Preliminary runs at low residence times resulted in conversions that were no higher than were obtained in the soaker. This same reactor will also be used for low pressure (500-1000 psig) operation with Illinois No. 6 coal.

Antisolvent Deashing

The recycle of deasher underflow enables the deasher to recover a large percentage of extract as ash-free feed to the LC-Finer. Twenty percent deasher underflow in the recycle solvent is comparable to a second pass through the SCT unit. The overflow/underflow ratio to satisfy this recycle requirement is, therefore, much lower than for Illinois No. 6 coal and easier to attain. In addition, the higher fluidity of the underflow has enabled the deasher to attain deasher bottoms with over 50% quinoline insolubles. As seen with bituminous coal, the preasphaltenes concentration in the underflow 850°F+ extract is significantly higher than in the overflow.

LC-Fining

In order to maintain 850°F+ extract conversions of 35% to 40%, the LC-Finer control temperature was raised to 730°F, and the space velocity was increased to 0.7. At this higher temperature, the product distribution is lighter, resulting from greater thermal cracking of the 650°F to 850°F fraction. All activities - conversion, heteroatom removal, preasphaltene reduction and hydrogenation - showed no unusual response to

the 30°F increase in effective temperature. Proton NMR analyses continue to show that the product is an excellent hydrogen-transfer solvent and that about 60% of the hydrogen that goes into the 650°F+ product goes into cyclic alpha or beta position. Conversion activity remains 2-3 times greater than for bituminous coals.

Upon starting the unit on November 28, after the Thanksgiving Day holiday, a rupture occurred in the feed preheater section. Only hydrogen was flowing through at the time of rupture, and prior to rupture, all line temperatures were below 200°F. There were no personnel injuries, and the damage was confined to the PDU equipment, which includes electrical power lines, thermocouple wires, instrument air lines, hydrogen rotometers, lines, and valves. The rupture line has been sent to the C-E metallurgy laboratory in Chattanooga, Tennessee, for an examination that may determine the cause of rupture. Mechanical repairs were completed in December. Electrical repairs will be completed early in January. As the result of the fire, the LC-Fining and SCT units did not operate in December.

Task 2 - LC-Fining PDU Support

Run 3LCF14 was completed. This run was made to determine the extent of solvent rehydrogenation in one reactor operating at the same conditions as 3LCF operated for Illinois No. 6, i.e., 740°F effective temperature, 2700 psig, and over a twofold range in space velocity. Hydrogen consumption was only about 1500 SCF/bbl, and conversions were about 20%. However, the 650°F+ product had essentially the same H/C ratio as achieved in the three-reactor train. These results indicated that solvent rehydrogenation occurs before conversion and that one LC-Fining reactor is sufficient to make a good SCT solvent. Proton NMR analyses and additional data interpretation are in progress.

Task 3 - Data Evaluation

Conversion activity of bench-scale runs in Subtask 2.1 indicate that activities were 25% higher in the first reactor. Run 3LCF9 was compared to 4LCF13, and increases in H/C ratio were the same, confirming the results of 4LCF14. Microautoclave tests with Illinois and Wyodak coals showed a decline in conversion below 1000 psig.

Task 3 - Deashing

The bench-scale deasher has been fabricated and installed. Operations were delayed until February due to lack of manpower.

Kerr-McGee Advanced Direct Coal Liquefaction

Three scoping runs were successfully completed on the 350 lb/day integrated bench-scale unit during this quarter. The primary objective of these runs was to evaluate subbituminous coal process options in terms of catalyst performance, distillate yields, and generation of coke precursors. The best results were obtained with an integrated two-stage liquefaction configuration, in which hydrotreated Light Deashed Resid (LDR)/heavy solvent was recycled with thermal Heavy Deashed Resid (HDR) to the first stage as slurry solvent. This particular configuration, which avoided feeding HDR to the hydrotreater, resulted in the least coke buildup and loss of surface area of the catalyst.

A batch-reactor test procedure for rapid evaluation of resids and catalysts in terms of coke precursors was also developed this quarter. The procedure developed closely simulated catalyst performance in continuous, larger-scale operations.

Results/Discussion Summary

The three runs conducted this quarter were specifically designed to allow meaningful inter-run comparisons that might contribute to the achievement of stated objectives. The same, but not necessarily optimal, operating conditions were used for all three runs. The primary variable was hydrotreater feed composition. As the hydrotreater feed was made progressively heavier with each succeeding run (LDR to full-range DR to HDR), overall distillate yields decreased, catalyst deactivation rate increased, and overall hydrogen utilization efficiency decreased. Average product yields of C₆ to -850°F liquids for the three runs ranged from a high of 49% for the hydrotreated LDR run to 38% for the hydrotreated HDR run. Fresh presulfided Shell 324 catalyst was used for each of the runs.

Future Work

Additional operation of the bench-scale unit is planned to confirm the results discussed above and to investigate some modification of operating conditions to further improve the liquefaction performance obtained with the Wyoming subbituminous coal. Some testing of Illinois No. 6 coal in selected modes of operations is also planned.

Rotating Disc Contactor Deashing — Foster Wheeler Energy Research Corp.

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. The program tasks are the following:

- Task 1 - Project Work Plan
- Task 2 - Obtain and Characterize Feed Samples
- Task 3 - Preliminary Batch Solvent Deashing Tests
- Task 4 - RDC Deashing Runs
- Task 5 - Project Management/Data Deliverables

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 (ITSL) process and to study the characteristics of the solvent at a variety of process conditions.

The continuous catalytic reactor system constructed by the Xytel Corporation (Xytel unit) was employed to hydrogenate the solvents required for Task 2, ITSL Solvent Quality vs. Degree of Hydrogenation. The goal was to extensively hydrogenate raw Koppers Heavy Residue Creosote Oil (KC-Oil) in order to obtain a wide range of hydrogen contents for experimentation. The hydrogen content of the raw KC-Oil was approximately 6.5 wt%. The catalyst used in the Xytel unit was a modified Shell 324 nickel/molybdenum (Ni/Mo) extrudate. A reactor temperature of 700°F produced a total liquid product with a hydrogen content of 9.5%, and a temperature of 750°F produced a total liquid product with a hydrogen content of 11.5%.

Raw KC-Oil is a material with a nominal boiling range of 500°F to 850°F. When it was hydrogenated in the Xytel unit, a substantial amount (20 to 30 vol%) of material was produced that boils below 500°F. The hydrogenated products were topped by atmospheric distillation to an initial boiling point of approximately 500°F. A distillation and a determination of hydrogen content will be performed on each topped product.

The raw KC-Oil solvent was subjected to SCT process conditions in the microautoclave in order to determine the effects of process conditions on the KC-Oil alone. For most of the runs, the H/C ratio of the solvent decreased from 0.86 to values ranging from 0.83 to 0.80. The solvent H/C ratio increased to values ranging from 0.92 to 0.95 in three of four runs made at two-minute residence time. This increase was due to an increase in the solvent hydrogen content from 6.52% to values ranging from 6.96% to 7.26%.

At the lower residence time of two minutes, some KC-Oil hydrogenation appeared to take place. As the residence time increased, the KC-Oil dehydrogenated. If coal had been present, some of this hydrogen could have been donated to the coal.

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.

Task 2 - Model Compound Studies.

The following additional information was obtained on the preparation and characterization of the model compound 1,4-dihydroxy-9,10-dihydroanthracene: (1) 52 g (49% of theoretical yield) was obtained in the form of fine, light-yellow needles from benzene. An additional 33 g (31% yield) was obtained from the benzene mother liquor on second crystallization, for a total yield of 80% of theoretical. The second crop was dark-yellow colored. (2) The product obtained from the first crystallization was positively identified by proton-NMR. The information is shown in Table 2. No other peaks were observed in the spectra. Determination of the melting point and completion of the elemental analysis remain to be done on this task.

Task 3 - Depolymerization.

Experimental work has been initiated with Illinois No. 6 coal and phenol-BF₃ to test the de-

Table 2.

Position	Chemical Shift (ppm from TMS)	Number of Protons
α^2 aliphatic	3.04	4
Aromatic (phenolic ring)	7.35	2
Aromatic	8.05 (center of A_2B_2) multiplet	4
Phenolic OH	13.54	2

polymerization technique and the product separation procedures. The first experiment, which was conducted at 100°C for 4 hr, is nearly completed. The second experiment, conducted at 120°C for 4 hr, is underway. After the completion and the evaluation of these experiments, depolymerization experiments with fluorophenol- BF_3 can begin. A direct fluorine probe will be acquired for the NMR instrument by the Science Center. After it is installed (early 1984), it will be possible to determine the amount of incorporated fluorophenol in the products by direct ^{19}F -NMR.

Task 4 - Characterization of Coal Extract and Solvent.

The 1H NMR spectra of the SCT recycle solvent distillate fractions have been obtained. Recording of the ^{13}C -NMR spectra and the evaluation of the data are underway. A brief inspection of the 1H NMR spectra obtained this far showed that the +750°F to 850°F fraction is much more aromatic in character than the -750°F fraction. Both fractions have strong absorptions in areas that are characteristic of hydroaromatic structures.

Task 6 - Dehydrogenation.

The apparatus was assembled for the dehydrogenation experiment. It consists of a glass flask equipped with a magnetic stirrer, a helium gas inlet port, and a reflux condenser; this is connected through a sample port/tee to a gas buret and leveling buret. A known amount of sample, together with measured amounts of solvent and Pd on $CaCO_3$ catalyst, is added to the flask. The system is purged with helium and sealed. Three experiments were conducted to check out the system with tetralin as a model compound. Since boiling of the solvent provides nucleation and the necessary agitation for H_2 gas formation, the experiments were carried out under "boiling-solvent" conditions. The following H_2 yields were obtained (expressed as % of theoretical) over a

period of 5 hr: with durene as the solvent (b.p. 197°C), 91%; with 2-methylnaphthalene (b.p. 241°C), 5%; and with quinoline (b.p. 238°C), 85%. The experiment with durene indicates that the use of a solvent somewhat below the boiling point of tetralin (b.p. 207°C) gives nearly theoretical conversion. The low conversion obtained with the higher boiling methylnaphthalene was probably due to the much reduced activity of tetralin in the liquid phase. The high conversion obtained with the high boiling quinoline is remarkable; it indicates that quinoline promotes this reaction by some mechanism.

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

Preliminary data from microautoclave scoping studies and bench runs 227-11,12 performed during the last quarter indicated that higher distillate yields were obtained at milder conditions than with existing single-stage technology. However, the even higher predicted distillate yields have not yet been achieved.

The uncertainty in comparing microautoclave results to bench run results and questionable data from BR 227-11,12, due to the numerous interruptions because of mechanical problems, led to a minor restructuring of the immediate test program. It was felt that longer bench runs would yield more meaningful data and also result in a cost savings by eliminating extra start-up and shutdown activities. Consequently three bench runs of 15-days duration were replaced by two bench runs of 23 days duration. Also a consistent and repeatable microautoclave procedure was developed so that microautoclave conversion results would be comparable. It was felt that this procedure may also lead to a better direct comparison of microautoclave/bench run results.

The major program task during this quarter was the performance of two 23-day bench runs. The

first run, BR 227-13, was planned around the lower first-stage temperature range, which gave the best microautoclave and BR 227-11,12 results. System pressure was held constant, and the second-stage temperature was varied, along with residence time, which was equal in both stages. In all, six operating conditions were investigated. The run was very smooth, with only one minor interruption. Preliminary results again indicated that higher-than-conventional but lower-than-predicted distillate yields were obtained at all operating conditions.

Some of the conclusions that can be drawn from the BR 227-13 results are the following:

- The first-stage temperature effect was insignificant over the range studied.
- Slightly higher than conventional distillate yields with an excellent hydrogen efficiency are obtained at milder conditions in terms of residence time and second-stage temperature.
- The best distillate yields were obtained at slightly more severe conditions in terms of residence time and second-stage temperature. However, this was offset by a higher C_1 - C_3 gas make and a reduced hydrogen efficiency.
- Only minor catalyst deactivation was noted over the duration of the run.

Hydrocarbon Research had originally recommended studying pressure effects in BR 227-14. However, after reviewing the data from BR 227-13, it was agreed that at this stage of the program it would be more beneficial to recheck the effects of first-stage temperature of a lower and broader range. Microautoclave testing indicated that almost comparable distillate yields may be achieved at an appreciably lower temperature range; and consequently BR 227-14, which was started in early December, was planned to cover these conditions. Additionally, if time permits, a new recycle technique would be tested at the last operating condition.

During the course of BR 227-14, which is still in progress, no improved distillate yields were obtained at the lower first-stage temperatures suggested by microautoclave studies. As a matter of fact, distillate yields were reduced and operating difficulties were encountered due to the increased viscosity of the recycle material at the lower temperatures. Therefore, run conditions were altered to retrace the temperature range that gave the best distillate yield. A meeting is planned in early January 1984 to review all microautoclave and bench run results and plan future testing.

Microautoclave procedures have been standardized. In addition, DOE has requested that HRI review excess government property and obtain a second high-temperature sand bath so that cool-down or heat-up affects between first- and second-stage temperatures can be eliminated.

Microautoclave testing of the catalyst effect in the first stage is underway. Side-by-side tests of thermal/catalytic first stage are being run to determine if a catalyst is required in the first stage. Preliminary results indicate that at the temperatures already tested, the catalytic first stage gives marginally better results than the thermal first-stage. Catalyst candidate testing in the microautoclave is also being done.

Engineering analysis to assist in evaluating the results of the new technology and develop preferred processing schemes has been ongoing. Other engineering efforts in terms of process optimization and evaluation of economics are planned, but DOE has requested that this effort be delayed until a reasonable understanding of process operating parameters is attained.

Cost versus work performed for data generated is falling in line. With the successful completion of BR 227-14, cost versus work performed will be in balance, with both being slightly lower than projected.

Disposable Catalysts

The goals of this R&D area are to evaluate the use of alternative inexpensive materials or low material concentrations as liquefaction catalysts for reducing technology costs and increasing liquid product yields and to test selected materials in continuous process units.

Research on Coal Liquefaction — Gulf Research and Development Company

Two-Stage Processing

Six experimental runs were conducted to examine the two-stage processing of an Illinois No. 6 bituminous coal. The first run consisted of an initial dissolution experiment at 842°F, 2250 psig, and 6.2-minute residence time to prepare a filtrate from the dissolved coal that could be further processed in a second-stage hydrogenation reactor. The second-stage reactor runs used either ground commercial catalyst (Ni-Mo on alumina) or pyrite as slurry catalysts. Three runs were conducted using the commercial catalyst, and two runs were conducted with pyrite. All the second-stage runs used 2.5% by weight of additive based upon total feed.

The second-stage runs were conducted at residence times of 2 hours at temperatures ranging from 779°F to 806°F. Use of the slurried commercial catalyst produces less total oil product (30% based on first-stage coal feed) than that that can be produced using a fixed bed of extruded commercial catalyst. Use of pyrite at the same run conditions produced even less total oil (23%). The heavy products produced in the second stage with the slurry catalyst were also of poorer quality (higher sulfur and nitrogen) compared to those obtainable with formed catalysts. Increasing the reaction temperature from 779°F to 806°F increased the hydrocarbon gas produced by about 3.5% while increasing the total oil produced to 40% for the slurried commercial catalyst and to 28% for the pyrite.

Short Contact Time Processing

Thirteen short-contact-time coal dissolution experiments were run using subbituminous coal under a variety of residence-time, slurry-recycle, temperature, and catalyst-additive conditions. Increasing the residence time from 5 minutes to 45 minutes at 820°F with 0.85% pyrite addition based on total slurry increased the hydrocarbon gas yield from 1.1% to 4.6%, increased naphtha from 0.5% to 7.0%, and lowered the insoluble organic matter from 18.8% to 8.8%. Total oil and resid yields did not experience major changes. An increase in reactor temperature from 808°F to 842°F decreased insoluble organic matter and increased hydrocarbon gas yield but produced scattered yield values for total oil and resid.

Three different catalysts were studied in the short contact time dissolution runs: pyrite, commercial cobalt-molybdenum on alumina, and ammonium-molybdate emulsion. At a 10-minute residence time and a temperature of 825°F, and with catalyst addition of 2.0% based upon slurry, pyrite gave the greatest conversion, followed by the molybdate emulsion. Hydrocarbon gas yields were equivalent with all three additives, and the total oil yield was highest with the pyrite and the commercial Co-Mo catalyst (20.0% and 19.5%, respectively).

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

A static-bed silica gel percolation column was designed and fabricated to scale up the preparation of modified solvents. The column has been used to treat an Illinois No. 6 coal-derived process solvent mixed with pentane (using a pentane to solvent ratio of 3:1). The silica gel to process sol-

vent ratio was 1.4:1. Elution of the column with methylene chloride recovered the N₂ and O₂ compounds adsorbed on the column. The adsorption and desorption cycle was repeated six times. The adsorption efficiency and the heteroatom removal activity of the silica gel column decreased significantly after the first cycle; however, they decreased only marginally in subsequent cycles. Stronger solvents for regenerating the adsorption efficiency of the silica gel column are being investigated.

To test the effect of grinding coal in the presence of molybdenum carbonyl and modified solvent at elevated temperatures in different atmospheres, samples of a 20 x 100 mesh fraction of Burning Star coal were ground, then liquefied in a series of runs to determine oil yields. When small amounts of either oil-soluble iron or pyrite and H₂S were used in the grinding step, oil yields of 40% to 45% were obtained - the highest to date.

Improved Dispersion Techniques for Slurry Phase Catalysis — Auburn University

In order to prepare highly dispersed metal sulfide catalysts, with negligible porosity and stable surface areas under coal liquefaction reaction conditions, high-surface-area nonporous supports will be employed. Methods such as impregnation, precipitation, ion exchange, carbonyl decomposition, and incipient-wetness impregnation were evaluated for their potential to yield highly dispersed metal sulfides of Mn, Fe, Ni, Ru, Mo, and W on nonporous substrates such as SiO₂, SiO₂•Al₂O₃, Al₂O₃, TiO₂, and MgO. Because nonporous supports will be used, only those preparation methods that involve strong substrate-metal bonds are useful and include (1) ion exchange, (2) impregnation using specific chemical reagents or carbonyls, and (3) carbonyl decomposition. Because metal carbonyls of the type discussed above can be linked chemically to a surface through available hydroxyl groups and/or will decompose if they contact a hot substrate, they provide a versatile path for preparation of a wide range of different metal sulfides using either porous or nonporous supports.

Appropriate glassware and preparation vessels have been ordered or are under construction. Saturated carbonyl solutions are housed in air-free buret-type addition funnels and can be added directly under an inert atmosphere or mixed at a desired lower concentration (also under an inert atmosphere). The carbonyl solution will then be transferred to a second vessel in order to contact

the support under an inert atmosphere. The support can be pretreated at temperatures up to 750K in various types of gaseous environments (or vacuum) before addition of the carbonyl solution. Once the carbonyl solution and support are in contact, they may be agitated or refluxed using an integral condenser in the support preparation cell. Following appropriate refluxing and/or contact, the solvent may be evaporated by thermal or vacuum methods. These vapors will be passed through high-surface-area heated vessels and then KOH solutions to decompose unreacted carbonyls and minimize safety hazards. Following solvent removal, the treated support can be pretreated in a variety of vacuum, gaseous, and/or thermal environments to stabilize the catalyst and prevent it from sintering or deactivating prior to use.

Selection of the above-noted preparation methods, as well as implementation of these schemes, has been made so as to choose procedures capable of employing a broad range of metal sulfides and supports. This broad range of methods is required to correctly gauge the effects of different metal sulfides and different catalyst structures during coal liquefaction reactions in slurry phase operations.

Advanced Preparation for Direct Coal Liquefaction — Battelle Columbus

Two coals were selected and obtained for experimental processing: an Illinois No. 6 bituminous coal and a Wyodak subbituminous coal. The Illinois coal sample, from the Burning Star No. 2 mine, had a measured chlorine content of 0.1%, which is less than that desired for processing through some of the advanced preparation techniques planned for use. Alternative coal sources are being examined to determine whether or not a higher chlorine content coal can be obtained for project use. In the interim, samples of both of the existing coals were ground (wet and dry) in laboratory equipment and sent for detailed analysis. Results from these analyses will be used to refine the planned coal preparation program.

Liquefaction Process Research and Technology Development

The goal of the R&D area is to 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.

Advanced Coal Liquefaction Catalyst Development — Amoco Oil Company

Task 6 - Two-Stage Optimization

Preliminary results from the first two-stage runs with Illinois No. 6 coal were encouraging because substantial improvement in yield and product quality over any one-stage process was achieved. In addition, results showed very little deterioration during the initial seven-day run.

The first two-stage run was made with a high temperature thermal first stage with a high residence time, and a low temperature catalytic second stage with moderate residence time. The pressure in both stages was 2500 psi, and the system was operated once through, with no liquid recycle. Substantial increases in toluene and hexane conversions, over optimal single-stage processes, were achieved and essentially no preasphaltenes or resid was produced. Heteroatom removal was generally higher.

In the second run, the residence time of the thermal first stage was lowered. Unfortunately the second run was terminated after only one day of operation due to a failure of the first-stage heater. However, results from the one day of operation indicated conversions equal to or higher than the first run had been attained.

Two-stage studies will be continued during the current quarter. First- and second-stage conditions will be varied based on results of tasks in an attempt to optimize product quality and yield.

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

Task 5 - Batch Screening

A number of new catalyst preparations, made by the latest process technology, were tested with coal and extract feeds. Active catalysts are in the group, and some have lower metals contents than base-line catalysts (Shell 324M and AMOCAT 1A)

Equations that correlate the results of initial catalyst screens were developed. The results indicate a mechanistic tie between catalyst performance in the two applications and suggest similar paths for further development.

Task 6 - Continuous Aging

Operations of the CSTR unit focused on establishment of thermal and catalytic base lines at various temperatures, flows, and slurry solids

levels. Also, one experimental bead catalyst was tested. The control system functioned as designed with 24-hour operations using only day-shift coverage. It was necessary to modify the product collection lines to extend the unit run time from 48 hours to more than 100 hours.

Initial results indicate that the presence of catalyst has little effect on the conversion of coal, and no catalyst aging is observed under conditions tested so far. Performance of the slurry solvent, a well-hydrogenated creosote oil, is implicated. Furthermore, thermal conversion of coal in a 33%-solids slurry is higher than in a 25%-solids slurry. Use of an alternate process solvent is being considered.

Supercritical Extraction of Coal — Gulf South Research Institute

The experimental apparatus planned for use in the conduct of the supercritical extraction experiments was assembled. Three initial experiments were conducted at subcritical conditions with ammonia to check out equipment and to establish some base-line results to act as subsequent reference points. Minor problems were identified in feeding the extraction fluid to the apparatus. These problems were corrected and will be followed by parametric studies at conditions ranging up into the supercritical range.

Characterization of Coal-Derived Components — University of Wyoming

Preasphaltene fractions from both Wyodak and Kentucky coal resids were obtained using the new chromatographic procedure involving aluminum oxide-Chromasorb T. The two preasphaltene fractions from each coal were submitted for elemental analysis.

In support of analytical studies being conducted at PETC, a neutral fraction of 650°F. product from the Wilsonville PDU was chromatographically separated by the number of double bonds. The resultant products were returned to PETC for analysis using high resolution mass spectrometry.

After extensive investigation of the optimum mobile phase for the separation of monohydroxy aromatics by reversed-phase, high-performance liquid chromatography, it was determined that a ternary mobile phase of acetonitrile:tetrahydrofuran:water at a volumetric ratio of 14.6:28.3:57.1 would yield the best separation. In this same work, the optimum mobile phase for the separation of dihydroxy aromatics was methanol:tetra-

hydrofuran:water in a volumetric ratio of 8.5:19.7:71.8. Work is continuing on the development of a technique for the separation of organic nitrogen compounds and of a general separation procedure for hydrocarbons, nitrogen compounds, and hydroxyl aromatics.

Liquefaction Support Activities — Sandia National Laboratory

Exploratory catalyst studies have focused on the development of tests to evaluate the activity of coal liquefaction catalysts. Reactions performed in batch microreactors have demonstrated that the hydrogenation of pyrene and 1,2,3,6,7,8-hexahydropyrene can be used to assess two catalytically important quantities: the intrinsic activity and diffusion resistance. Results show that just two experiments, one with powdered catalyst and the other with whole extrudates or beads, can be used to define the hydrogenation rate constant, k , and the effective diffusivity, D_e , of the reactant in the catalyst pellet. In addition, these parameters can be used to assess catalyst deactivation. For example, comparison of presulfided with aged catalyst (50 lb SRC/lb catalyst) from the Wilsonville facility showed that although k for pyrene hydrogenation was the same ($5.9 \times 10^2 \text{ min}^{-1}$) for the two catalysts, D_e for the aged catalyst was a factor of 5 less than that of the presulfided fresh catalyst (3.3×10^7 vs. $1.5 \times 10^6 \text{ cm}^2/\text{sec}$). This indicates that pore plugging or fouling, rather than active site poisoning, is the primary deactivation mechanism.

Activity testing of fresh and aged catalyst samples from Wilsonville run 242 has been carried out in an atmospheric model compound testing unit. The results on whole aged extrudates (as compared to fresh catalyst) showed a 35% loss in hydrodesulfurization (HDS) activity and a 58% loss in hydrogenation (HYD) activity following presulfiding, and additional losses when coal processing began. Whole extrudates from the end of the run (527 lb SRC/lb catalyst) showed no measurable activity, whereas the same catalyst pulverized to minus 200 mesh had 46% HDS and 33% HYD compared to fresh catalyst. This activity increase due to smaller particle size suggests that diffusional limitations are important causes of deactivation. The observed activity losses were correlated with the rapid buildup of organic deposits and the slower rate of increase in contaminant metals.

Samples of fresh Shell 324 were aged at 350°C by flowing Wilsonville hydrotreater feed through pellets contained in a microflow reactor. Sim-

ulated distillation analysis of effluent samples indicated little or no upgrading of the feed to distillate product. The catalysts were subjected to analysis for coke (600°C volatiles) and elemental composition. Metal distribution on the most highly aged sample (150 g feed/g catalyst) was determined by microprobe analysis. Catalyst deactivation was determined with a high-pressure (500 psig H₂) model compound test reactor at 350°C using dibenzothiophene for hydrodesulfurization, indole for hydrodenitrogenation, naphthalene for hydrogenation, and dibenzofuran for hydrodeoxygenation. Decreases in activity, relative to fresh catalyst, were observed as a function of catalyst age. For example, hydrodesulfurization activity decreased 98%, and hydrogenation activity decreased 91% for the most highly aged samples. Regenerating the catalyst by firing at 600°C increased the activity to approximately that of the fresh catalyst.

Measurements of the hydrogen content of the insols obtained from liquefaction of Wyodak coal in indole at several conversion levels indicate that hydrogen is not shifted among the products. This further supports the hypothesis that liquefaction of Wyodak coal in indole proceeds by a hydrogen bond disruption mechanism rather than thermal covalent bond rupture followed by radical capping with hydrogen. Additional evidence for this liquefaction mechanism is that Wyodak conversion in indole reaches a plateau after 20 minutes, while conversion in a typical hydrogen donor solvent continues to increase with time. The plateau would be expected where no further reactions could occur after solvent access to the coal had been complete.

The high-temperature and high-pressure helical screw rheometer (HSR) is fully operational. Continuous viscosity vs. temperature measurements from 5000 cp at 23°C to 57 cp at 105°C were demonstrated for a Newtonian viscosity standard (Cannon S-2000) at shear rates from 100 to 1000 sec⁻¹ and 0 to 1300 psig. The HSR-derived viscosities were within ±10% of the standard viscosity data. Testing of the HSR will conclude with a well-characterized power-law fluid, after which the slurry-gelling study will be initiated.

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 acceptability and compatibility with conventional fuels.

Refining and Upgrading of Syntfuels — Chevron Research Company

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.

The ITSL light oil and the middle distillate from Illinois No. 6 coal (Burning Star Mine) were blended in the ratio recommended by Lummus to represent whole liquid product when operating at 650°F cut point. Inspections of the blend indicate that the actual end-point was closer to 700°F than 650°F. Present bench-scale pilot plant work uses this 700°F end-point blend as feed. The feed was water-washed to remove chlorine prior to its use; the first water-washed batch (WOW 4998) was used up recently, and a second batch (WOW 5104) was prepared.

At DOE's request, Chevron also redistilled the blend to obtain a 650°F end-point feed for pilot plant comparisons with the 700°F end-point material. In the first part of this distillation, the 550°F-fraction was separated from the higher boiling fraction. The bottoms will be transferred to a smaller column, in which the 550°F to 650°F fraction will be taken overhead; the latter overhead fraction will then be combined with the "Start"-550°F fractions to make the "Start"-650°F feed.

Lummus also sent Chevron two partial drums (about 65 gal total) of heavy distillate to represent additional product obtained when the ITSL process is operating at 850°F cut point. However, this material contained a considerable amount of 850°F+ heavy oil and had an extremely high metals content. Most of the metals were not removed when the heavy distillate was filtered through a 3-micron filter; therefore, an attempt was made to redistill the heavy distillate in a continuous vacuum distillation column to separate the material boiling above 850°F. Chevron's distillation laboratory reported that after the column was lined out and about 40 lb of overhead material had been obtained, the column suddenly plugged solid with a cokelike material. Examination of the remaining undistilled material revealed that the interior walls of the shipping drums were coated with a tarlike deposit and some solid particulates, suggesting that the oil was unstable

and some polymerization had occurred in the drums prior to the attempted distillation. The plugging may be the result of additional thermal degradation in the column.

Bench-scale Pilot Plant Run 90-167 involving the hydrotreatment of 700°F-ITSL oil using Chevron's ICR 106 catalyst continued logging 5370 hours on stream. The first 150 hr were made with a petroleum-derived start-up feed; the next 5220 hr were made with the ITSL oil. With a hydrogen partial pressure of about 2300 psia (2500 psig total pressure), tests were made at three liquid hourly space velocities (LHSV): 0.5 LHSV (150-1760 hr); 1.0 LHSV (1760-3420 hr); and 1.5 LHSV (3420-4190 hr). Total volume of ITSL oil processed at this pressure was 3645 volumes per volume of catalyst (3481 grams of ITSL per gram of catalyst). Results of 0.5 LHSV and 1.0 LHSV were described in detail in Quarterly Report FE-2315-92. Some additional detailed product yields and properties of very narrow boiling fractions of product obtained at 0.5 LHSV and 1.0 LHSV are presented in Quarterly Report FE-2315-96, Tables II through VI. The test at 1.5 LHSV was started at 750°F. Product nitrogen lined out at about 2.5 ppm. The temperature was increased to 760°F after 250 hr at 750°F. Product nitrogen dropped to 0.4 ppm. No fouling was noted during the next 500 hr at 760°F. Yields and product properties for this period of operation at 1.5 LHSV are given in Tables VII-X in Quarterly Report FE-2315-96.

After 4190 run hours, the pressure was decreased 500 psi to 1800 psia hydrogen pressure (total pressure to 2000 psig) to accelerate the catalyst deactivation rate. Chevron has studied the catalyst deactivation rate at this pressure and LHSV (1.5) for other coal-derived liquids, and therefore will be able to compare results. The temperature was held constant at 760°F. At these conditions, the test was continued for 810 hr. Product nitrogen lined out at 6 ppm, and little or no catalyst deactivation occurred. The chemical hydrogen consumption during this period was about 575-600 SCF/bbl. Only limited information is available at this time on product properties for the test at 1800 psia, and inspections will be given in a later report.

After a total of 5000 run-hours, the pressure was decreased to about 1500 psia hydrogen (1700 psig total pressure) to further accelerate the catalyst deactivation rate. Once again, the LHSV was held at 1.5, and the temperature at 760°F. Product nitrogen at the conditions lined out at about 24

ppm. The chemical hydrogen consumption was about 375 SCF/bbl. After 100 hours at these conditions, the temperature was raised to 780°F to increase the nitrogen removal. Product nitrogen decreased to about 6 ppm. At 5170 hr, the feed drum was changed to another drum of the ITSL oil, WOW 5104. Within about 20 hr, the pilot plant began to experience plugging problems, which were traced to the reactor section. At first the plugging was believed due to coking in the preheater. At 5370 hr, the reactor was cooled and depressured, and the preheat section was cleaned. Shortly after restarting, however, plugging occurred again. The problem was finally traced to a water-soluble material in the reactor outlet line that, upon analysis, turned out to be ammonium chloride. Although the feed had been water-washed to less than one part per million of chlorine, the feed in this particular barrel upon analysis still showed 210 ppm of chlorine. It is not known how the barrel became contaminated, and the feed is being water-washed again to see whether the contaminant can be removed. Because almost all of the tests planned for the run had been completed, and because the catalyst may have been coked in a nonrepresentative manner due to a lack of hydrogen flow during the periods of plugging, a decision was made to terminate run 90-167. The catalyst is being held for possible future use.

A second 500-hr hydrotreating bench-scale pilot plant run (Run 86-75) of hydrotreated 700°F-ITSL middle distillate was made to prepare a sufficient quantity of 350°F+ hydrocracker feed for future hydrocracking studies. Bench-scale Pilot Plant 86 was operated with three reactors in series, containing a total of 750 mL of ICR 106 catalyst as compared to 130 mL of catalyst in Run 90-167. Conditions for the run were 715°F to 720°F, 1.0 LHSV, 2300 psia hydrogen (about 2500 psig total pressure), and 8000 SCF/bbl recycle gas rate. At lined-out conditions, the product contained less than 0.5 ppm nitrogen and was considered to be a suitable hydrocracker feed. The run is now complete, and the product is being analyzed prior to blending. Further cracking of this product to naphtha would be necessary if it were to be reformed and marketed as gasoline.

In the next quarter, a hydrocracking test run on hydrotreated 350°F+ ITSL oil prepared in Pilot Plant Run 86-75 is scheduled. A brief test to compare the hydrotreating of 650°F-ITSL oil with 700°F-ITSL oil will also be made.

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).

Engineering Development

The goal of this project area 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, and heat and seed recovery systems.

Slag-seed interaction runs were continued at the Coal-Fired Flow Facility (CFFF). The LMF1E series (slag screen removed) was completed and data for this series, as well as the previous LMF1D series (slag screen in place), are being analyzed for inclusion in a future report. Installation of the air-heater and superheater components was begun and specifications for procurement of a baghouse were drafted, reviewed, and made final. Normal winter shutdown took place at the end of this reporting period.

Reports for the Heat and Seed Recovery System were prepared for presentation to the Electric Power Research Institute MHD Review Board on December 5. The following documents were also prepared: Topical Report on the development of a one-dimensional code to predict the thermal behavior of the University of Tennessee Space Institute MHD radiant furnace; a Test Report on the LMF1A&C series of tests; a Safety Analysis on the CFFF; and an Ambient Air Quality Base Line for the CFFF.

The AVCO Everett Research Laboratory (AERL) is continuing to perform high magnetic field, supersonic MHD channel tests. The purpose of these tests is two-fold: (1) to simulate early-commercial channel operations in the regimes being recommended by the Advanced Power Train Program and (2) to look for and study magnetoaerothermal (MAT) phenomena predicted

by the STD Corp. Operating regimes (4 Tesla, supersonic) for the experimental investigation of MAT phenomena were defined (in coordination with STD). Initial tests have been completed at AVCO, and these data are being used by STD in their computer programs to predict the occurrence of MAT phenomena. The MK-VI facility is being prepared to proceed with a second series of tests to increase the interaction parameters defined by STD to optimize the chance of seeing the MAT phenomena most clearly. An improved analytical model to account for cathode wall nonuniformities was also developed to improve design capabilities.

Extensive use was made of the three-dimensional temperature distribution computer program code to optimize the electrode/insulator geometry. Geometry improvements will minimize the leakage current and maximize both electrode and insulator life. These computer studies aided the development of two new concepts for sidewall design. One of the sidewall concepts was constructed and tested for four hours in the MK-VII channel. Visual observations show minimal wall erosion and indicate that more test time is justified. The second concept is in the initial manufacturing stage.

Bench-scale studies have been started to determine the reason for cathode metal loss. Initial indications are that it is an electrical process, most probably inter-cathode arcing.

Four basic current control type circuits with new semiconductor devices were tested at AVCO. These circuits have undergone initial debugging and testing on a simulated four-electrode channel and on four electrodes of the MK-VII channel. These devices result in circuits that are simpler, more reliable, and more energy efficient.

The High Performance Demonstration Experiment (HPDE) at Arnold Engineering Development Center (AEDC) has been halted indefinitely by severe damage to the magnet's Force Containment Structure (FCS). The undamaged components are being stored until a decision is made by DOE to rebuild the FCS or terminate the project. The high-interaction tests at AVCO will provide information upon which PETC can evaluate the need for rebuilding the HPDE. A decision concerning future work at AEDC should be reached by the end of FY84.

Work is continuing on the close-out of the GE CDIF superconducting magnet subcontract at the MIT Francis Bitter National Magnet Laboratory. The status of the Superconducting Magnet Technology Program was presented at an Electric Power Research Institute MHD Evaluation Board meeting on December 5, 1983. A five-year MHD Magnet Technology Development Program Summary Report was submitted to PETC for review. Efforts by MIT continued on a structural design for a superconducting magnet and a high-current conductor study/program definition.

Work continued at the Argonne National Laboratory (ANL) on the evaluation of CFFF data for NO decomposition, and studies were performed on NO kinetics in the FEUL (Fossil Energy User's Laboratory) facility. Pyridine addition to the fuel was used to study NO formation. Additions of about 0.7% nitrogen to the oil increased NO concentration in the gas by about 410 ppm. The conversion percentage of nitrogen in pyridine to NO decreased from 50% at 0.7% nitrogen in oil to about 30% at 3.5% nitrogen in oil. Nitric oxide decompositions with temperature were measured as the gas cooled through the test train. These data are being compared to values calculated by the NASA kinetics code.

Analysis of the CFFF LMF1C series test data was completed by ANL, and a literature search was conducted on reaction rate constants for the NO reactions. A report on this effort is in preparation. Calculations using the COMMIX code were continued by ANL to estimate gas-flow paths in the CFFF radiant furnace. These calculations are intended to predict mass flow distributions around the slag screen, and heat flux distribution in the radiant furnace.

The fabrication of all components for the first (slagging) stage of the 50-MW(t) coal combustor was completed by TRW this quarter. Hardware assembly, proof and leak testing, and component flow calibration were completed in early December. All first-stage hardware (including vitiator and slag tank) was shipped to the TRW test site and installed on the test stand in late December. Plumbing of the appropriate feed systems to the major components has been initiated. Detailed design and fabrication of secondary items, such as a Performance Evaluation Module (PEM) and seed injectors, are 90% complete. A detailed test plan for 50-MW(t) testing at TRW was completed.

Determinations by TRW show that Montana Rosebud coal samples of approximately 7% moisture and 60% minus 270 mesh prepared by

the CDIF are satisfactory for their characterization tests. Shipments of approximately 270 tons of prepared coal have started from the CDIF to TRW. Use of this coal will permit the test program at TRW to be structured to use a common injection and distribution coal system without the requirement for duplicating this development at the CDIF.

Supporting Research

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

Pacific Northwest Laboratory (PNL) is conducting research to select materials for use as the ceramic current lead-out between the refractory cap and the copper supports in future advanced MHD channels. Indium oxide and tin oxide are used as additives to the refractory cap materials to increase the electrical conductivity. Compositions containing the two materials have resulted in conductivities greater than the conductivities of either of the individual materials. The highest conductivity obtained, so far, is for compositions containing between 54 mol% and 65 mol% In_2O_3 .

Fabrication techniques for the In_2O_3 - SnO_2 compositions have been developed that result in sintered powder densities between 92% and 96% of theoretical. The constraint on the fabrication is that the densities are obtained by sintering at temperatures no greater than 1875 K for times no greater than twenty hours.

Samples of $\text{SnO}_2 \cdot \text{In}_2\text{O}_3 \cdot \text{PrO}_3 \cdot \text{HfO}_2$ have been prepared with densities near 90% of theoretical. Several samples have been corrosion-tested in coal slag. Examination of the post-corrosion test samples show that In_2O_3 is the least corrosion-resistant material. Testing and examination are continuing.

The major efforts at Stanford University during this quarter focused on analytical modeling. Good agreement has been obtained between a theoretical model and MHD channel pressure fluctuations measured in experiments conducted at the Stanford M-2 test facility. The model is based on a one-dimensional analysis of the MHD flow train and predicts the frequency spectrum of the magnitude and the phase of the pressure fluctuations. The measured and calculated resonant frequencies are in very good agreement.

Development work on a computer code for prediction of rod electrode current distributions is now complete. This code will be used to compare

predicted current distributions with experimental measurements and to study current distribution sensitivity to variations in the temperature and velocity fields.

Also in progress at Stanford is a study to further refine the non-equilibrium model used to predict the absorption of potassium seed by slag. The seed concentration profile near the electrode wall will be investigated using a two-dimensional boundary layer code adapted for study of the diffusion of seed toward the slag. Most of the work this quarter was concerned with the validation of the computer program. Further modifications will be needed before the code can be used to calculate the fraction of potassium lost to the slag. All pertinent data on diffusivities of potassium species are being gathered.

The development of non-interference diagnostic instrumentation continued at the Mississippi State University.

Construction of a hollow cathode light source for use in characterization of critical NO source parameters progressed. Calibration measurements for the optical NO system were started using a flat flame burner. Several tests of the CARS System were conducted to determine the effect of laser intensity on the nitrogen CARS spectra; results indicate no substantial effect over the intensity range tested. A laboratory burner and a particle-injector system were completed for tests of CARS system on particle-laden flows.

A signal processor and computer interface for the Particle Size Distribution System was tested and analyses necessary for interpretation of test data were continued. Modifications of the 16 bit I/O board of the Potassium Emission/Absorption System were completed and work continued on synchronizing the chopper and detector.

In support of the national MHD Program, plans were continued for the integration of several field-ready instruments. These will be reduced in size and operated by a central minicomputer.

Systems Engineering

The goal of this project area is to obtain the engineering data base required for the design, fabrication, and operation of MHD power trains for power plants sized at approximately 200 MW(e).

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, General Electric (GE) completed all efforts under Task 1 of Phase 1. Briefly, the effort on this task included the analysis of 200-MW(t), 500-MW(t), and 1000-MW(t) MHD/steam plants, and a critical evaluation of MHD technology state-of-the-art. The report for this task was published, and results of Task 1 were presented to the GE Utility Advisory Board. Task 2, Definitions of MHD Advanced Power Train Design Approaches, was initiated with Subtask 2.1, Detailed Generator Studies. This work includes investigation of performance optimization effects, ash carry-over and slagging effects, loading and controls, channel/magnet coordinated design, life-limiting mechanisms and durability, fabrication techniques and assembly, and repair/replacement and maintenance.

A revised Task 1 draft report was prepared by Westinghouse for the APT project, and work in Task 2 was initiated. Major activities underway in Task 2 include work on detailed channel design and the study of various power consolidation circuit designs. Progress on the 200-MW(e) scale generator design study conducted by the STD Research Corporation was reviewed on December 19. Within the constraints and conditions given to STD, the supersonic generator appears more attractive, on the basis of power production (costs were not considered), than the subsonic generator at this scale. The aforementioned results were obtained using a quasi-one-dimensional analysis.

At STD, computer analysis of AEDC/HPDE Run No. 16 was completed. The computed results are in good agreement with measured data. An accurate prediction was obtained for both the strength and threshold of the magnetoaerothermal effects observed in Run 16.

Support by STD of the high-interaction MHD experiments at AVCO continued. Input data necessary to perform accurate computer simulations of the MK-VI channel were further refined. A test case was computed using conductivity and channel operating conditions corresponding to those of the August 16, 1983, experiment at AVCO. Good agreement was obtained between predicted and measured shock locations and other gas-dynamic parameters.

Component Development and Integration Facility (CDIF)

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

In this reporting period, work at the CDIF focused on the testing of the coal grinder/drier system. The objective of the tests was to determine whether Montana Rosebud coal containing nominally 30% moisture could be dried to nominally 5% moisture using existing equipment. The results of the test were promising; 287 tons of coal, processed in 60 to 70 ton batches, was dried to approximately 6.5% to 7.5% moisture. The coal produced in these tests has been shipped to TRW, where it will be used to fire the 50-MW(t) coal combustor.

Modifications necessary to permit installation of the 50-MW(t) coal combustor (and ancillary

hardware) in the A-Bay of the Operations Building will begin in January 1984. Modifications to the coal processing equipment to permit drying from the 6.5% to 7.5% range to the 5% moisture level will also be instituted during this same period.

Closed-Cycle Systems

The goal of this project area is to develop a technology base for a highly efficient, coal-fired, closed-cycle MHD power plant with inherent environmental and economical advantages over currently installed and operating fossil-fuel-fired electrical generation systems.

Closeout of the existing closed-cycle contract with General Electric was started and PETC property management personnel began disposal procedures for the hardware from the Valley Forge Facility.

ALTERNATE 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. (CE)

Analyses of the data from the second-level washability studies and the CWM vendor slurryability evaluations concluded that only one of the twenty candidate coals met all of the selection criteria. The other nineteen coals either had poor washability or poor slurryability. As a result of the difficulty in making CWM with most of the previously selected coals, the CWM vendors submitted data on twenty-one coals they consider good for CWM. Gulf Research and Development Company (GR&DC) has begun compiling data to check these coals for suitability for the project.

The CWM vendors showed reluctance to meet our CWM specifications and agree to the warranties; therefore, new specifications were developed to satisfy both producers and users.

Discussions were held with CE and GR&DC regarding the problems associated with making slurry with cleaned Lower Kittanning coal. A theory concerning the surface properties of Lower Kittanning coal is being formulated, and Dr. Parfitt of Carnegie-Mellon University will assist GR&DC in analyzing the surface property differences of run-of-mine and beneficiated Lower Kittanning coal.

Samples of cleaned Splash Dam coal were sent to five CWM manufacturers for analysis and processing into 20-gallon batches; GR&DC will characterize the resultant samples, which were of good quality. Splash Dam coal has been selected to be the reference coal.

Two CE burners were selected, one for tangential firing and one for wall firing. The tangential burner is similar to CE's standard oil burner. The wall-fired burner is the design developed for and tested at Uppsala Kraftvarne, Sweden. The atomizer for both burners has previously been tested on three different CWM's at firing rates from 15 to 80 x 10⁶ Btu/hr. Fabrication of both burners was completed. A final recommendation on the remaining burner suppliers will be made in the near future.

Atomization tests were conducted on a single-cell version of the CE atomizer. Preliminary results indicate good atomization using the Splash Dam reference CWM. Preparations are underway to test the CE tangential burner in the Small-Scale Burner Facility (SSBF). The CE wall burner is scheduled to be tested after the tangential burner evaluation.

Fireside Performance Test Facility (FPTF) tests with Lower Kittanning CWM were completed. Tests were conducted at average peak furnace temperatures of 2800°F and 2950°F. No major problems were observed during handling or combustion of slurry. Flame stability and carbon burn-out were very good during the tests. Ash slagging and fouling behavior were very low. Ash deposition was comparable or even lower when firing Kittanning CWM at similar conditions, compared to the dry pulverized Kittanning coal. Convection tube erosion rates were very low during all testing. Furnace performance calculations were run for one of the utility steam generator study cases to compare furnace temperature versus load to the FPTF test conditions. Preparations are underway to test Splash Dam CWM.

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

The low-pressure transfer system is essentially complete. Approximately 95% of the high-pressure loop piping has been installed. All of the major equipment has been delivered.

Test loop fabrication and installation have been completed. Installation of instrumentation and controls will be completed by the end of January. Equipment and instrumentation calibrations will begin in mid-January.

The CWM's for testing at TRW's Capistrano Test Site (CTS) will be transported across country by truck in 3000-gallon tankers. It is possible that these slurries will be subjected to conditions that may facilitate phase separation.

Four parameters will be measured periodically: temperature, vibration, density at various liquid levels (ΔP), and samples for solids loading tests. Samples will be obtained from three designated liquid levels every twelve hours. These samples will be tagged and later analyzed for solids content if it is apparent that settling has occurred. In order to predict the amount of settling caused by vibration, temperature extremes, etc., data from

this analysis should correlate with other information gathered.

Conversion of Oil-Designed Boilers to Dual Coal-Oil Firing — Burns & Roe, Inc.

The draft of the Final Report is being prepared for submission to DOE/PETC for review.

Deposition Test Program for Micronized Coal-Water Mixture Fuel — Stone & Webster Engineering Corp.

Occidental Research Corporation (ORC) prepared the last 185 barrels of micronized coal-water slurry (CWS) fuel for the Northeast Coal Utilization Program (NECUP). One hundred and seventy-nine barrels were sent to Babcock & Wilcox and 6 barrels to the Adelphi Research Center.

The Adelphi Research Center (ARC) performed additional particle size distribution tests and determined that 97% of the particles were smaller than 44 microns. This is in substantial agreement with the measurements made by ORC. In addition, ARC made the necessary preparations to their test loop to permit performance of the slurry pumping tests.

Babcock & Wilcox performed the remaining fuel characterization tests (free swelling index, sulfur forms, and elemental ash analysis), repeated the droplet size distribution tests for the commercial (5×10^6 Btu/lb) atomizer, and performed characterization tests of the Laboratory Ashing Furnace (LAF) atomizer.

Advanced Combustion Concepts

Contract negotiations were completed with TRW for their "Advanced Slagging Coal Combustion System" project, and negotiations with AVCO will be completed for their "Retrofit Slagging Coal Combustion System" project in the near future.

Cost Estimating Algorithms for Evaluation of Advanced Combustion Systems — Gilbert Associates, Inc.

The Final Report and associated computer software were submitted to DOE. A draft CA/CB Addendum Report, including a User's Guide, was submitted to DOE for review. The review was completed by PETC, and the comments were submitted to Gilbert.

***Development of a Vortex Containment
Combustor for Coal Combustion Systems —
Energy and Environmental Research Corp.***

The approach is to use an isothermal flow model to address the key design parameters for the prototype vortex containment combustor. The key parameters to be investigated include geometry scaling, fuel injector design, slag drain design, and air slot arrangement. Designs of the isothermal flow model have been initiated.

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

The objective of this project is to prepare a conceptual design of an Integrated Superfine Coal Combustion System and evaluate its technical and economic feasibility for converting oil-fired steam generators to coal firing. A survey of the existing related literature was made. Work has begun to identify and review the candidate system, as well as to select the system for conceptual design analysis.

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

The project objective is to determine the feasibility of using pulse combustion for advancement of coal utilization. The contractor began a literature search and a review of prior efforts. Preliminary technical considerations, with respect to the size and type of applications and regarding the type of pulse combustor configurations (aerodynamic, flapper, rotating disc), were identified. Criteria and parameters will be formulated on the basis of these considerations.

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

A manual literature search was used to develop the optimum strategy for updating the com-

puterized literature search. As a result, the computerized search resulted in approximately 800 references. Direct contacts were made with Zimpro, Ontario Research Foundation, Stanford Research Institute, and Dickinson Pure Air Combustion. These meetings led to additional data, which have just been released or are in preprint form.

Initial data review indicates a lack of solid engineering design information in the literature. While much of the work has been done on a proprietary basis, discussions with process developers indicate that design techniques lean heavily on empirical techniques. There appears to be sufficient information to establish a design data base and to identify critical data gaps. Further efforts under this task will be aimed at establishing the nature of each.

A meeting was held with Zimpro to define process and economic information that could be made available. Zimpro has experience in the reactor portion of the system and will be one of the alternative reactor technologies evaluated. Process and economic information on the Wetox reactor technology was obtained in a report from Ontario Research Foundation. Only limited information is available on the supercritical reactor technologies, since these are not as fully developed.

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

The project includes critical experiments to show viability of impact separator technology for two modes of operation; the first is operation in the fouling temperature regime (<2000°F), and the second is operation in the slagging temperature range (>2600°F).

Initial sizing estimates of the impact separators, for operation downstream of Solar's pilot-scale coal combustor facility, are in progress. Alternative layout schemes for the impact separator test modules are now under study.

FLUE GAS CLEANUP

E.W. Evans, Cost Account Manager

R.A. Carabetta, Chief, Coal Utilization 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 pro-

duced 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.

Representatives from Research-Cottrell and Argonne National Laboratory visited PETC on October 5, 1983, to discuss Microwave Excitation for Combined NO_x/SO₂ Flue Gas Cleanup. Both felt that the microwave approach should be more efficient and less energy intensive than either the E-Beam or glow discharge approach. Microwave should also require less protection for personnel than the E-Beam.

Representatives from Physical Sciences, Inc., visited PETC on October 25, 1983, to discuss the possibility of making a unified assessment of radiation-initiated NO_x/SO_x emission control technologies. Among other things, this study would compare energy requirements, efficiency, costs, etc., for such types of processes as the E-Beam, glow discharge, microwave, and laser/lamp. Such a study could be very useful in comparing several of these types of processes already included in the flue gas cleanup program.

A paper describing and giving the status of DOE's Flue Gas Cleanup Program was presented at the EPA/EPRI Flue Gas Desulfurization Symposium held in New Orleans, La., November 1-4, 1983. The paper was well received by the approximately 800 to 900 attendees representing utility and industrial users, vendors, and Federal and State Governmental agencies.

Start-up of the Research-Cottrell E-Beam/Spray Dryer Combined NO_x/SO_x Project at the TVA's Shawnee Steam Plant had been held up for approximately two months awaiting a representative from High Voltage Engineering on-site to check out the E-Beam gun installation. Checkout is now underway, and shakedown tests are scheduled to begin about mid-January 1984.

A meeting was held at PETC on November 8, 1983, with Ebara International Corp. to review the E-Beam/Ammonia Injection Project at Indianapolis Power and Light's E.W. Stout Plant. A draft of the work plan was briefly reviewed and will be formally submitted. Ordering of the long delivery equipment items has been started.

A Flue Gas Cleanup Program Review with DOE Headquarters personnel was held at PETC on November 16, 1983. Both DOE in-house and contract efforts were reviewed, with emphasis on proposed follow-on efforts for the NOXSO process evaluation. A cooperative effort in-house at PETC, similar to the current Wheelabrator Frye arrange-

ment for testing an ESP on the spray dryer, is being considered.

A meeting with SMC was held at PETC on November 22, 1983, to review their task on "Comparative Analysis of E-Beam NO_x/SO_x Processes." The study is incomplete, but SMC reports that prospects for utilizing the mixture of ammonium nitrate and ammonium sulfate from Ebara's E-Beam/ammonia injection process as a fertilizer material appears unlikely. Representatives from Penelec also attended a portion of the meeting to review their flue gas cleanup efforts and DOE's Fluidized-Bed Copper Oxide tests. If Penelec is receptive to the idea, one of their plants could become a site for follow-on efforts for the FBCO or NOXSO processes.

A meeting was held at PETC on November 30, 1983, with Pittsburgh Environmental Systems, Inc., to review problem areas regarding their subcontract with NUS (the prime contractor with DOE on evaluation of the Sulf-X Process). During the discussion it appeared that the problem was primarily one that NUS was not properly flowing down some of the provisions included in the prime contract. The contracting officer will direct NUS to flow down those provisions in dispute to the subcontractor intact. This should resolve the major problem areas and permit the signing of the NUS subcontract with Pittsburgh Environmental Systems, Inc.

Representatives from Ceramatec, Inc., and the Jet Propulsion Laboratory presented a briefing at DOE Headquarters in Germantown on December 15, 1983, describing a unique approach for simultaneously controlling SO₂ and NO_x. The approach utilizes a zirconia electrode cell to break down SO₂ and NO_x to elemental sulfur, nitrogen, and oxygen. Representatives from PETC attended the meeting to discuss the pros and cons of such an approach.

Work plans were received for review, and ordering of equipment was started for the following new projects:

- Glow Discharge Irradiation Process Evaluation with Westinghouse R&D Center, Pittsburgh, Pa., in response to the PRDA for Advanced Combined NO_x/SO_x/Particulate Control Processes.
- Moving-Bed Copper Oxide Process Evaluation with Rockwell International, Canoga Park, Calif., also in response to the PRDA for Advanced Combined NO_x/SO_x/Particulate Control Processes.

- Zinc Oxide in Spray Dryer Process Bench-Scale Tests with Battelle Columbus Laboratory, Columbus, Ohio, also in response to the PRDA for Advanced Combined NO_x/SO_x/Particulate Control Processes.

- Zeolite Catalyst Process Bench-Scale Tests

with Science Applications, Inc., San Diego, Calif., also in response to the PRDA for Advanced Combined NO_x/SO_x/Particulate Control Processes.

- Carnegie-Mellon University Unsolicited Proposal for a Systems Study of Integrated Environmental Control Technologies.

COAL PREPARATION

E.W. Evans, Cost Account Manager

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

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.

Southern Illinois University Cooperative Agreement

The Department recently negotiated a Cooperative Agreement with the Coal Research Center of the Southern Illinois University at Carbondale, Illinois (SIU-C). This Agreement is entitled "Operating Agreement for the Use of the Coal Technology Laboratory and a High Sulfur Coal Research Project."

The overall objective of this effort is to conduct a broad-based research program on high sulfur coal and thereby expand the technology that will allow for the increased use of this coal in an environmentally acceptable manner. As part of the Agreement, SIU-C has established the Coal Technology Laboratory at the site of the former Carbondale Mining Technology Center. The technical program of the Agreement consists of eleven projects covering four areas: coal science; coal preparation; coal conversion; and coal utilization.

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 synergistic effects of blending such coals.

Fine Coal Washability Evaluations of Alaskan Coals

The University of Alaska has completed centrifugal float-sink testing of seven samples. Data will be evaluated and reported after receiving chemical and physical analyses of the samples. (University of Alaska)

Fine Coal Characterization Evaluations of Western Region Coals

The University of North Dakota is fabricating a metal float-sink centrifuge flask to alleviate the problems they have encountered with glass flask breakage. Centrifugal gravimetric work is continuing on the Western Region samples. (University of North Dakota Energy Research Center)

Identification and Evaluation of Mineral Forms as Related to Trace Elements in Washed Coals

Emphasis during this period continued to be on the low-temperature ashing of the coals selected for determination of mineral matter and on correlations of this mineral matter content with the trace- and major-element data from the previous phases of this study.

Initial examination of low-temperature ashing of these samples focused on optimization of instrument variables to obtain the desired ash in the time frame allotted to this project and, at the same time, on keeping the temperature in the ashing chambers at a minimum to accomplish oxidation of the coal matter with minimal changes in the mineral matter. That effort continues. The refuse-type fractions containing little car-

bonaceous material are being ashed, as expected, at a much more rapid rate than are the clean and ultraclean coal samples that are high in carbon content.

Additionally, there was the need to examine the characteristics, in particular, the particle size of the low-temperature ash produced, to determine whether further pulverization would be necessary to prepare the samples for IR and X-ray analyses. Eight samples were selected for this initial examination, and the data showed that the particle size of the ashes obtained by low-temperature ashing thus far appears to be adequate for the subsequently scheduled IR and X-ray analyses.

The X-ray diffractometer for use on this project was purchased and delivered. A Dranetz Series 606 Power Line Disturbance Analyzer was installed by the manufacturer (Phillips Electronic Instruments) on August 23 to monitor the line voltage to the laboratory. A clean line voltage source is a requirement prior to installation of the diffractometer to ensure the attainment of valid data. In order to accomplish this, two voltage stabilizers, an RFI filter, and a line voltage regulator were ordered and installed for use with the diffractometer. The diffractometer was also installed during this time, and initial minor problems were corrected by the manufacturer.

Work has been initiated with the X-ray diffractometer. The initial work involved standard materials to select the best sample preparation technique, as well as the optimum instrument and data measuring system parameters, and to generally familiarize the operator with this diffractometer system. (Bituminous Coal Research)

Microcharacterization of Mineral Matter Components in Coal

In order to address the association of mineral matter with coal, the automated-image analysis system required upgrading to permit execution of state-of-the-art image analysis software. All the necessary hardware for the system has been received. The basic computer components have been assembled and are operating properly. Interfacing between the new computer and the scanning electron microscope is now complete. Work will soon be finished on interfacing to the automatic stage control on the SEM. New software interfaces are being developed for the energy- and wavelength-dispersive X-ray analyzers, and preliminary tests are underway to verify proper operation of the software. Minor problems that have been identified are being addressed,

and accuracy of the new algorithms is still being evaluated and should be established in January.

Results are still being evaluated for the pair of raw and cleaned blends of Dietz No. 1 and No. 2 coalbed samples reported previously. Comparisons are being made between analytical results for the different sample preparation techniques. In addition, the raw coal is being submitted for X-ray diffraction analyses in order to determine the aluminum-rich phase found previously in the AIA study. (Ames Laboratory, Iowa State University)

Ashing Properties of Deep-Cleaned Coals

Low temperature ash concentrates have been completed for the Illinois No. 6 and the blend of Dietz No. 1 and No. 2 bed coals in both the raw and the super-cleaned state. Petrographic analyses of the LTA concentrates are completed, and the fusion testing under argon atmosphere has begun. The data from these experiments are being evaluated.

In order to test the reactions of the LTA concentrates to high temperature under reducing and oxidizing conditions, a furnace has been secured and is being installed. The furnace will be modified to accept ASTM-specified gas flows.

A fully quantitative X-ray diffraction technique is being developed to provide a convenient means of analyzing an LTA concentrate for seven crystalline species. This experimentation, beginning with grinding techniques and extending through sample-mounting procedures to a complex computer program, is proceeding well. It is intended in this study to produce a program that can be used by an experimenter familiar with X-ray powder diffraction work and having minimal experience with computers to quantitatively analyze a mixture of seven phases without extensive training. Publication quality data should be obtained on the first run. The present program is nearing that state of excellence, and it is being modified to include seven phases instead of the present three.

An experimental low temperature asher is nearly completed and is in the process of testing on a limited basis. It is the objective of this study to permit completion of ashing without breaking vacuum for the purposes of agitating the coal. (Ames Laboratory, Iowa State University)

Photoacoustic Spectroscopic Analysis of Fine Coal

Activities of this newly initiated project have included the following: (1) a review of the literature

on the infrared analysis of whole coal, (2) exploration of sample preparation methods appropriate for monitoring coal during beneficiation processing, (3) acquisition of preliminary IR spectra on a range of coal types in unprocessed and processed states, and (4) selection of a new post-doctoral staff member who will assume a major role in the project beginning in January 1984.

Sample preparation methods have been explored for qualitative, semiquantitative, and quantitative analyses that involve varying degrees of preparation complexity from simple drying to spray deposition of thin layers of coal prior to photoacoustic analysis. Spectra have been acquired using these methods on samples from the Ames Laboratory and Exxon coal libraries and on samples from coal processing.

During the next quarter, these spectra will be analyzed in terms of surface oxidation, mineral composition, and other properties important to beneficiation processing. Research will be expanded to encompass samples from coal-dewatering processes. (Ames Laboratory, Iowa State University)

Characterization of Western Coals

Los Alamos National Laboratory has reviewed existing data (combined with a cost-benefit analysis) in order to formulate a detailed plan for sampling the strippable coals of New Mexico. All proposed drill sites have been plotted on maps, with the exact sites to be determined by a surveying team prior to actual drilling. Drill site spacing was based on potential strippability of coals (thickness, depth, inclination of beds) where geologic information was available, and on "best guess" where less information was available. Primary emphasis will be placed on the coals of the

San Juan Basin (where drilling will begin) and secondarily on the Raton area and the smaller fields within New Mexico. The total number of sites to be drilled for this project has been estimated to be about 300. Responsibilities for supervising the drilling, logging, core description, sample collection, and packaging have been assigned. Costs, methods, and types of logging, coring, and surveying have been determined. (Los Alamos National Laboratory)

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.

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.

Results of the surfactant screening tests to date have shown that Aerosol OT-100, an anionic wetting agent, was the most suitable additive to test in the Heavy-Liquid Cyclone (HLC) pilot plant as a means of counteracting the deleterious effects of high amounts of surface moisture on the feed coal.

Four pilot plant tests were run to examine the effects of moisture and additives in an HLC. The operating conditions and preliminary results are summarized in Table 3.

The two-inch cyclone was operated using Freon-113 with 28 mesh x 0 coal. The 10% solids concentration in Test No. 2 was a departure from Test No. 1, where the solids were 20 wt%, but was

Table 3.
Preliminary Results of HLC Tests

	Test 1	Test 2	Test 3	Test 4
Coal Size, mesh	28 x 0	28 x 0	28 x 0	28 x 0
Surface Moisture, %	1.7	1.5	10.0	10.0
Solids Concentration, %	20	10	10	10
Inlet Pressure, psi	85	85	85	85
Coal Feed Rate, tph	3.5	1.75	1.75	1.75
Additive Concentration, lb/ton	0	0	0	10
Clean Coal Ash, %	7.3	13.2	20.9	7.6
Refuse Ash, %	77.9	83.0	66.4	84.1
Clean Coal Yield, %	69.4	77.3	80.4	72.0
Efficiency Index	741	486	255	797

necessary due to the "roping" that was observed in the underflow. The system was operated with an inlet pressure of 85 psig, which produces a flow rate of 45 gpm. It is unclear why the clean coal ash in Test No. 2 jumped from 7.3% to 13.2%. A lower solids loading usually produces better results. This is still being studied, and it may be that the system is very sensitive to moisture changes of even 0.2%, which was the case here. Test No. 3 shows the effect of 10% moisture in the feed. The clean coal ash went from 13.2% to 20.9%, and the efficiency was very low. In Test No. 4, however, the addition of 10 lb/ton of Aerosol OT-100 caused the clean coal ash to drop back to 7.6%, and the separation was as good as in Test No. 1.

Each test sample is undergoing a washability analysis to determine the final performance of the cyclone in each case. Next quarter, tests will be run with ultrafine coal ($20\ \mu\text{m} \times 0$) and with lower specific gravity liquids (1.3-1.4). In addition, froth flotation comparison tests will be run. (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.

This new project was initiated at the beginning of this quarter. A batch, 1-inch pressure cell was fabricated for running tests at 850 psi; test procedures were experimentally determined; and the equipment was tested. The results of two preliminary tests showed that a difficult-to-clean Upper Freeport ROM coal was cleaned from 35% ash to 10% ash, and a clean coal from Illinois was further cleaned from 8% ash to 2% ash. Testing will continue next quarter.

A continuous, 3-inch cell is being designed and will be fabricated next quarter. It will be upgraded and modified based on the experience gained from working with the 1-inch cell.

Also, a laboratory bulk density measuring device is being designed and fabricated. It will be used to measure the absorption of liquid CO₂ by coal under pressure.

The main physical properties of the liquid CO₂/H₂O/coal system to be investigated have been identified as phase equilibrium data, density data, interfacial properties, and viscosity. The major experimental variables to be studied are slurry concentration (5% to 50%), particle size ($20\ \mu\text{m}$ to 500

μm), feed ash content (5% to 35%), agitation speed (0 rpm to 2000 rpm), residence time (0 sec to 600 sec), and pressure (800 psi to 950 psi). (University of Pittsburgh)

Pilot Plant Continuous HGMS Testing

The objective of this project is to demonstrate at the pilot plant level the technical and economic feasibility of beneficiating fine coal via a continuous high-gradient magnetic separation (HGMS) process.

Parametric testing of the pilot plant continued this quarter; however, preparation plant downtime has continued to be a major source of delay in the testing. Preliminary results of the tests that have been completed thus far show ash reductions of 21% and 37%, and sulfur reductions of 14% and 20% at Btu recoveries of 92% and 81%, respectively. The reductions are not as high as originally anticipated. Several possible causes, such as air entrainment in the matrix or chemical contamination of the processing water, have been cited, and testing is now underway to investigate solutions to these problems. The tests originally scheduled with the first matrix have been completed. However, testing will continue with this matrix until satisfactory results can be achieved. Tests utilizing a second matrix have been postponed.

A computer program was written to compile and analyze the raw test data. Also, the froth flotation circuit at the preparation plant was sampled in preparation for the second phase of testing, which will make a direct comparison between HGMS and froth flotation. (Tennessee Valley Authority)

Mechanisms for Selective Coalescence

An investigation of the basic mechanisms that underlie various coalescence processes for beneficiating fine-size coal has gotten underway in this new project. A literature review is almost complete, and various experimental techniques that can be used for studying the surface chemical properties of coal and the inorganic minerals associated with coal are being reviewed in order to select the most appropriate techniques. Several methods that have been identified for measuring the wetting behavior of coal are the sessile drop method, the capillary pressure method, and the immersion time method. While the first method requires working with a smooth coal surface that may be 1 sq. cm. in extent or larger, the other techniques can be applied to fine particles. Methods for measuring the electrokin-

etic properties of coal particles and for investigating the kinetics of flocculation are also being reviewed. A light-scattering technique is one of the methods that may be used for measuring flocculation rates of dilute suspensions. For more concentrated suspensions, it may be possible to measure the rate of coalescence by observing the rate of change of apparent viscosity of the suspension. (Ames Laboratory, Iowa State University)

Fused-Salt Process Development

The Gravimelt reactor was utilized to produce approximately 1,000 pounds of coal-caustic float material that will be used as the raw material for performance of washing and reagent regeneration studies. Also, the stability of metal sulfides in fused caustic, contained in a nickel vessel, was tested in order to provide confidence that experimental equipment would be available for the regeneration studies.

In order to determine the effect of water on fused caustic desulfurization and demineralization of coal, a technique was tested and validated for the reduction of water in fused caustic to a level of 0.1%, calculated by difference, by using a combination of heating and purging for approximately 20 hours. No standard analytical techniques exist for the direct determination of water in caustic, but indirect methods were identified by contacting a caustic producer and the ASTM. (TRW)

Caustic Regeneration and Instrumental Characterization

Progress was made in identifying the problem of incomplete desulfurization during regeneration of the caustic wash solutions. Previous work has shown that although model solutions (containing only Na_2S plus NaOH) could be decreased by 90% in the total sulfur content by stripping with a mixture of CO_2 and N_2 gases at 90°C , the same procedure applied to real samples of caustic wash waters resulted in decreasing the total sulfur content by only 50%. At the same time, a grayish black precipitate was formed that was only about one-half organic in nature; the rest consisted mostly of Fe, K, and Si, with traces of Al, Cr, Ni, Pb, Rb, S, and Ti. Furthermore, it appeared that during this treatment with CO_2 and N_2 , all hydroxide was converted to a mixture of carbonate and bicarbonate before any sulfide was removed as H_2S . This indicates that considerable effort will be necessary in subsequent recausticization of the residue.

The nature of the sulfur species in actual caustic wash solutions was determined using titrimetric, spectrophotometric, and polarographic techniques. Immediately after filtration, as much as 50% of the total sulfur exists as polysulfides; the rest exists as sulfide, with small amounts of persulfide. Storage of the solution, even in sealed containers, results in rapid disappearance of the persulfide traces, leaving only sulfide and polysulfide. Exposure of the solutions to air or treatment of the solutions with hydrochloric acid or a mixture of CO_2 and N_2 gases eliminates the sulfide (either by oxidation to polysulfides or removal as H_2S gas, respectively) and leaves only polysulfides. Thus, it can be concluded that the previously proposed regeneration scheme can remove sulfur from the caustic solutions only if it is present as sulfide, leaving polysulfide untouched.

Additional experiments were performed by treating different coals with molten caustic in order to prepare samples of caustic wash waters for the studies described above and to optimize conditions for the removal of sulfur and ash. For a Pittsburgh No. 8 coal (8 mesh x 0) containing 3.12% sulfur and 7.02% ash, more thorough washing, using larger quantities of water and preheating the wash water to about 100°C , improved the removal of sulfur and ash by an additional 13% and 11%, respectively, to an overall removal of 78% and 85%, respectively. Subjecting the coal to a second cleaning resulted in a product with only 0.38% sulfur and 0.30% ash (removals of 88% and 96%, respectively). Similar removals could be obtained with an Illinois No. 6 coal (4.10% sulfur and 13.26% ash) if it was ground to minus 60 mesh before a single treatment (resulting in a final content of 0.57% sulfur and 0.56% ash). (Ames Laboratory, Iowa State University)

Trace Elements Removal

In this newly initiated project, the literature search on the modes of occurrence of trace elements in coal has been completed. Based on the reviewed literature, it is evident that modes of occurrence vary considerably, although several generalizations can be made.

Many elements of environmental concern, including As, Cd, Hg, Pb, and Zn, generally associate with the mineral portion of the coal and tend to be found along with the pyrite or accessory sulfide minerals. These minerals often occur, at least partially, as finely disseminated grains. The elements As and Hg have been observed to be in

solid solution in pyrite (FeS_2), while Cd can occur in solid solution in sphalerite (ZnS).

Although most trace elements appear to be largely associated with the inorganic components, several of them have a strong affinity for the organic portion of coal and are believed to be present as chelates. Among the elements in this category are B, Be, and Ge.

Physical cleaning methods do not adequately remove finely disseminated minerals or organically bound elements, thereby necessitating the use of chemical treatments for removing many of these constituents. The general superiority of chemical extractions as opposed to physical separations is apparent from the data available thus far in the literature. Simple leaching procedures utilizing various acids seem to be effective in removing many of the trace elements of interest, and these techniques will be investigated further on a variety of coals before employing more complex chemical treatments. (Ames Laboratory, Iowa State University)

Microwave Interaction with Coal

This new project addresses the mineralogical and petrographic study of changes in the mineral matter associated with coal after it has been subjected to microwave treatment. It is the intent to identify the mineralogical changes and to understand how they are brought about. In order to optimize the microwave desulfurization process, representative coal samples will be examined at several stages before and after microwave treatment.

The initial project activities in the past quarter include a literature search, arrangements of equipment and facilities, and discussions with other researchers involved in microwave desulfurization. All available literature was obtained on mineralogical and petrographic changes in the coal-associated mineral matter subjected to microwave treatments and to similar (but non-microwave) treatments. The literature search also involved a detailed review of documents pertaining to the microwave coal desulfurization process. Arrangements for equipment and facilities necessary to provide representative coal samples at different stages of the process were initiated. A mineralogist, who has been invited to Ames as a visiting scientist to evaluate the mineral phases before and after various treatments, will arrive in early January. (Ames Laboratory, Iowa State 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 a deep-cleaned coal product of consistent quality.

Fundamental Study for Improvement of Dewatering of Fine Coal/Refuse

Work to improve the dewatering of minus 35-mesh coal by vacuum filtration has been extended to include a study of the combined effect of using a long-chain anionic polymer flocculant and a nonionic surfactant. Two types of tests were run: (1) The flocculant and the surfactant were added simultaneously to a prepared coal slurry prior to filtration; and (2) the flocculant was added alone prior to filtration, and a surfactant solution was then used to wash the dewatered filter cake. In the first method, little or no improvement in dewatering was observed, i.e., the final cake moisture content was about 20%. On the other hand, when the second method was used, the cake moisture was reduced to less than 9%. (University of Pittsburgh)

Ultrafine Grinding of Coal in an Attrition-Chemical Reactor

Micropulverization tests are underway to establish operational parameters and accrue base-line data. Two coals have been selected for study: Upper Freeport bed coal from the Alpine mine in Grant County, W.Va., and Illinois No. 6 bed coal from the River King mine No. 1 in St. Clair County, Ill. The coal samples are being pulverized in a Union-Process Model 1-ST attrition mill using 3/16-inch stainless steel balls and, for comparison, in an 8-inch-long jar mill using randomly sized stone media. Particle-size determinations are made periodically throughout a run using a wet screening device. A Leeds and Northrup Microtrac instrument has been assembled and is being tested for later use in measuring the size distribution of the ultrafine particles. (Ames Laboratory, Iowa State University)

Dewatering of Coal by Pressurized Electroosmosis

The objective of this project is to increase the pore water pressure within a pressure filter cake by electrokinetic means and thus accelerate the removal of water. Since electroosmotic pressure acts only on the fluid phase and not on the solids, effective stresses to consolidate the solids do not

develop if an external stress or pressure is not applied.

This project consists of two phases: (1) bench-scale studies under various electrokinetic potential gradients and external pressures with slurries prepared from coal pulverized to various sizes, and (2) the development of a continuous-dewatering process using a belt filter press with a simultaneous applied voltage gradient. The bench-scale equipment has been designed and manufactured during this reporting period, and bench-scale studies should be completed within one year. (Ames Laboratory, Iowa State University)

On-Line Pyrite Monitor for Coal and Coal-Water Slurries

The continuous pyrite monitor has been moved to the Ames Laboratory coal preparation plant. The time of instrument operation has averaged approximately 25 hours to 30 hours per week during the first part of this reporting period. Pittsburgh seam coal, Illinois No. 6 coal, and Iowa coal have all been run through the instrument on a regular basis. Despite problems encountered with failure of water hoses and plant temperatures above 90°F, the instrument has continued to operate. The disk memory previously employed in the laboratory version of the instrument is now being replaced with a more durable bubble memory. Some difficulties have been encountered in bringing on-line the new DEC 11/23 computer system.

In the laboratory phase of the project, ten gallons of a commercial coal-water slurry mixture have been received, and a test stand is being constructed to examine this material using X-ray diffraction techniques. Preliminary coal slurry shakedown experiments will be carried out. This effort will also include the utilization of a more durable position-sensitive multidetector to sense diffracted X-rays. (Ames Laboratory, Iowa State University)

On-Line Alkali Monitor

The purpose of this task is to adapt the existing instrument, which has previously been employed for continuous on-line alkali measurement of gasifier and combustion effluent streams, to utilization in various chemical coal-cleaning processes. Three coal samples with alkali contents expected to be representative of typical feed and product stream compositions were selected. They are (1) Illinois No. 6, (2) Kentucky No. 9, and (3) a product sample from the TRW Gravimelt process. A representative suite of solid and liquid samples

for subsequent laboratory investigation have been prepared and are now available.

Both wet and dry methods of introducing the candidate coals, ground down to a size of 400 mesh, into the flame zone of the spectrometer are presently being explored. Work is also underway on development of a burner design more appropriate to the combustion of liquid and solid samples, as opposed to a gaseous sample. (Ames Laboratory, Iowa State University)

Ultrasonic Comminution

Prior to the beginning of the quarter, a contract was signed to initiate Phase II of this project. This effort will involve continuous operation and detailed testing of a newly designed auger array, as well as the eventual construction and testing of a 5- to 10-fold scaled-up version of the smaller unit. An improved redesign of the present ultrasonic auger grinder configuration will be finished in January or February. This new configuration should theoretically be more suited for continuous operation and also result in a lower comminution energy consumption.

An Illinois No. 6 coal with a low Hardgrove grindability index and a Upper Freeport seam coal with a high Hardgrove grindability index were selected for the test program. These coals are regarded as prime candidates for utilization in the coal-water mixture combustion test program. Efforts are underway to resolve questions relating to formulating an acceptable test matrix design, performing reliable particle size distribution measurements, and developing a mathematical model for scaling up the experimental test results. Correlations must be developed between key independent variables, such as ultrasonic power input, activated surface area, and auger rotational speed, and major independent variables, such as energy consumption, product size distribution, and grinding capacity. (Energy and Minerals Research Company)

Preparation of Low-Rank Coal

Construction of the hot-water/coal drying process development unit was continued. The building construction, equipment salvage, work platform, and slurry mixer support structure were all completed in this quarter.

Three cold-charge hot-water drying autoclave tests were performed using 1/4" x 3/8" lump Indian Head lignite. One test was made at 350°C, with the coal slowly cooled in water after 15 minutes at temperature. The second test was per-

formed at 300°C, with the coal rapidly cooled by vaporizing the water and venting the steam. The third test was made at 310°C, with the coal slowly cooled in water. Preliminary findings indicate that the two methods of cooling had little effect on the equilibrium moisture (30°C, 96% to 98% relative humidity) for the dried coals, as illustrated in Table 4.

The product gas and wastewater analyses of the three cold-charge hot-water drying autoclave tests were completed. The product gases consist mainly of CO₂, ranging from 90.6 mol% to 93.6 mol%, with methane being the next largest component (3.0 mol% to 5.6 mol%) and with trace

amounts of ethane, hydrogen, hydrogen sulfide, and ammonia. The wastewater analysis indicates that phenolics, methanol, and acetone are twice the concentration level for the 350°C run compared to the lower-temperature runs (300°C and 310°C); the runs slowly cooled in water are much more alkaline than the rapidly cooled run. This coincides with the Inductively Coupled Atomic Plasma (ICAP) elemental analysis results in Table 5, which indicate much higher concentrations of calcium and sodium in the wastewater for the slowly cooled runs compared to the rapidly cooled run and coal washed with distilled water at room temperature. (University of North Dakota Energy Research Center)

Table 4.
Effect of Cooling Method on the Equilibrium Moisture of the Dried Coals

Run No.	Drying Temp., °C	Method of Cooling	Equilibrium Moisture, wt%
1	350	Slowly in water	10.2
2	300	Rapidly by water vaporization	14.4
3	310	Slowly in water	11.3
Raw Coal	—	—	33.0

Table 5.
ICAP Elemental Analysis Results of Wastewater (mg/L)

Run No.	Drying Temp. (°C)	Cooling Method	Al	Ca	Fe	K	Mg	Na	Si
Wash	—	—	1.8	9.3	0.7	4.5	1.5	196	5.0
1	350	slow	<0.1	122	0.1	11.2	11.8	874	8.1
2	300	rapid	<0.1	0.4	0.1	0.9	0.1	2.1	<0.1
3	310	slow	<0.1	126	0.2	9.1	17.4	947	7.4

Expansion of Coal Preparation Plant Simulation

Work is currently in progress on altering the mainframe version of the simulator to accommodate overall water balancing within the plant. Several of the modules have been altered to allow makeup water to be added, in prescribed quantities, to the washers, screens, classifiers, and blenders. A new module is being developed for a thickener, which recycles water from dilute refuse slurry. An overall water balance is also being added to the entire plant.

The washer module has been expanded to include a Batac jig and a Dyna-whirlpool vessel. In

addition, a new and more extensive set of Baum jig distribution data has been added. This work is now complete. An investigation of the use of statistical distribution functions to represent the distribution data, in place of extensive tabular data now in use within the simulator, is planned.

Work is progressing on the development of a continuous-thickener model. This work is complicated by the need to coordinate efforts with the overall water balancing; nevertheless, the work is progressing satisfactorily. In addition, several refinements have been added to the module that is used to determine the moisture content of

saturated coal streams. This work will continue through the next several quarters.

The IBM Personal Computer model XT, with a 10-megabyte hard disk, was delivered early in October. A telephone connection has been established with the University of Pittsburgh main-frame computer. Some difficulty with the Fortran compiler that was purchased for the micro-computer has been encountered. These problems should be resolved within the next several weeks. Actual microcomputer compilations are expected to begin within the next few months, with this phase of the work well under way by summer. (University of Pittsburgh)

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 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

A PRU test using a 7-wt% peat slurry was made. Over 1,500 pounds of slurry were fed during a 4-hour period that included approximately 1½ hours of steady operation. Nominal reactor operating conditions were 400°F and 400 psig. Slurry, condensate, and gas samples taken during the test were sent to the analytical laboratories for analyses. The results of this test will be reported when they become available. The wet-carbonized peat slurry was saved for work in Task 2.

Two water flow tests were performed prior to the slurry test to permit tuning of control loops. In order to improve level control, the computer scan rate of control points was increased from once every 5 seconds to once every 2 seconds. Flash

heater level tap lines were relocated and nitrogen purges added to prevent liquid from collecting in the lines. These changes resulted in smoother operation of the flash-heating system.

The site and specifications for harvesting the peat for this program were finalized with the Minnesota Department of Natural Resources. Three contractors were contacted and two submitted verbal quotes. The lower of the two quotes was selected pending a firm written quote.

Seven wet-carbonization tests in the Batch Autoclave Unit (BAU) using peat from North Carolina were conducted during this quarter. The purpose of these tests was to expand the data base for North Carolina peat wet-carbonization tests started in an earlier program.

Task 2 - Product Water Processing

The design of the acid-phase and methane-phase digesters was completed. Materials procurement has begun and appropriate drawings have been submitted for bids on machining and fabrication. The design for activated sludge and oxidation pond treatment systems is being finalized. Site preparation was completed.

Slurry samples obtained from the PRU test were stored in freezers at IGT. This material will be used for acclimating a newly inoculated digester to thermophilic temperatures. (Institute of Gas Technology)

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.

The design and construction of the IRC will be done by the subcontractor (AMI), while operation and testing of the unit will be done by the contractor (IGT) in Chicago. This unit will be instrumented

adequately to evaluate the effects of significant operating parameters on product moisture content, throughput, and operability.

The assembly of a laboratory-scale unit has been delayed for about one month because of the modification on design. Laboratory tests will be started in February. (Institute of Gas Technology)

Prepare a Compendium of Information About Peat

The objectives of this contract are as follows:

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. Demonstrate that DOE has significantly reduced scale-up risks through its sponsorship of

these methods at the critical (early) stages of development, and set forth what must be done by the private sector in order to address the key issues impacting commercial feasibility.

3. Identify technical, economic, environmental, and social issues that must be addressed in conjunction with peat use in the United States.

During this first quarter, effort has been concentrated on the acquisition of information for the compendium. Three questionnaires were prepared, which requested information regarding the technical, environmental, and economic risks to the commercial utilization of peat for energy applications. The contractor has received 13 completed questionnaires and has been notified that additional responses can be expected shortly. The study team has begun to review the information from the survey. (Peat Systems International Corporation)

ADVANCED RESEARCH CONTRACTS

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

The objectives of the Advanced Research Contracts Branch are to (1) develop a program of research and exploratory development in coal liquefaction and combustion of coal and coal-derived fuels through contracts and grant awards to university, industrial, not-for-profit, and National research laboratories, (2) provide competent Project Managers for the contracts and grants, and (3) promote technology transfer through publication of the research results.

Reaction Chemistry

S. Akhtar, Coordinator

The objectives are to (1) identify the chemical reactions and their sequences in coal liquefaction by isotopic tracer techniques, ESR measurements, and model compound research, and (2) explore catalytic and noncatalytic techniques for direct and indirect liquefaction based on new concepts in coal science and catalysis.

An Illinois No. 6 coal was reacted with CO/H₂O at 400°C and 3,500 to 5,000 psig at an initial pH adjusted in the range of 7.0 to 13.3 by adding KOH. The reaction time was varied from 20 to 180 minutes, and the rate of disappearance of CO monitored by analyzing gas samples. Conversion of coal to THF solubles was determined by analyzing the product mixture on cooling. The results

show that both the disappearance of CO and conversion of coal are promoted by KOH and that a portion of the KOH is consumed irreversibly by the coal during the reaction. However, significant coal conversion was observed even when no KOH was added if the reaction time was long enough. (SRI International)

Recycle oil generated from an Illinois No. 6 coal in the Lummus ITSL process was vacuum-distilled into a -454°C fraction and a +454°C fraction. Each of the two fractions was then analyzed for total N and basic N. The -454°C fraction contained 4.41% total N, of which 2.08% was basic. By contrast, the +454°C fraction contained only 2.47% total N, of which 0.84% was basic. Clearly, in coal liquefaction products, the nitrogen concentration does not increase as fast as the carbon number, so that the N/C ratio decreases with increasing molecular weight. (Battelle Columbus Laboratory)

Coals can be solubilized by heating them with high-vapor-density, supercritical pyridine. Although pyridine is not as effective as aliphatic amines, a conversion of 75% can be obtained at 350°C in 4 hours. If the reaction is carried out using some D5 pyridine in normal pyridine, exchange of hydrogen and deuterium on pyridine is observed in the presence of coal, demineralized coal, or pyridine extract of coal, but not in the

absence of coal. Clearly it is some pyridine-coal reaction or interaction that leads to the scrambling. A mixture of coal, pyridine, and tetralin was studied to see if the good hydrogen donor tetralin would inhibit the reaction. Tetralin had no effect on the hydrogen-deuterium exchange. Remarkably, no deuterium was incorporated into the tetralin. This is strong evidence for a very specific exchange process. (University of Tennessee)

A fast atom bombardment (FAB) ionizer has been installed and is being tested for its capability to directly analyze liquid or solid preasphaltene-rich tar films. The FAB technique does not require the sample to be in the gas phase and therefore shows promise as a soft-ionization method for examining highly polar and labile non-volatile molecules such as those in preasphaltenes. (University of Utah)

Studies on the reductive cleavage of carbon-sulfur bonds in acid solutions with potassium iodide have shown that trichloroacetic acid and trifluoroacetic acid are much better reducing agents for 1-phenylthio-2-naphthol than formic acid is. Because trichloroacetic acid has a high boiling point (197.5°C) and relatively low cost, it is the solvent of choice for reductive cleavage of less reactive aryl sulfides, i.e., the 1-naphthol compared to the 2-naphthol compounds. (University of Massachusetts)

Thermochemical comparisons of five solid acidic materials (silica gel, sulfonic acid ion-exchange resin, Rawhide subbituminous coal, Texas big-brown lignite, and Illinois No. 6 bituminous coal) were performed after measuring the heats of immersion of these solid acids in 10 to 15 basic liquids at 80°C. (Duke University)

The influence of macerals from several bituminous coals on H/D exchange between tetralin-d12 and diphenylmethane was examined. The sporinite-rich exinites were the most effective promoters of the exchange reaction, followed by vitrinites, alginites, and the semifusinite-rich inertinites. Sulfur-containing compounds in the macerals enhance the promoting effect of the macerals on exchange reaction. (University of Chicago)

Exploratory Development *S. Akhtar, Coordinator*

The objectives are to (1) determine the relationship of coal characteristics to liquefaction behavior and (2) determine the preferred operating

regimes for liquefaction processes and obtain design data.

The rates of removal of organic sulfur and oxygen from two very reactive high-sulfur bituminous coals during liquefaction in tetralin were compared. The rates of removal of organic sulfur were similar to the rates of removal of organic oxygen. Thus, it appears that labile thioethers and ether cross-link bonds break up at comparable rates. The rate of removal of pyritic sulfur differed significantly between the two coals. Pyrrhotites are eventually formed from the pyrites in both coals. The difference in the rates of reduction of the pyrites may indicate a difference in their catalytic activity. (Pennsylvania State University)

Equipment has been installed to permit pressurization and agitation during reaction of coal with hydrogen in the presence of a perfluorocarbon liquids. Future experiments will limit the reaction temperature to 350°C because it was earlier found that higher temperatures produced a decomposition of the perfluorocarbon. (Emory University)

Attempts to solubilize an Illinois No. 6 coal by phenylation with BF_3 and AlBr_3 in benzene under ultrasonic irradiation at temperatures up to 80°C were unsuccessful. The solubilities of the products in benzene and pyridine were no different from those observed in a blank run. (Iowa State University)

Gas holdup and bubble size measurements were conducted in experiments with a 33-cm-i.d. column using air and carboxymethylcellulose solution in water. The gas holdup data were obtained by a bed expansion method, while the bubble size distribution was determined by taking photographs with a boroscope at different radial and axial positions. Gas holdup decreased with carboxymethylcellulose concentration and exhibited a maximum when plotted against superficial gas velocity. The bubble size measurements showed that the bubbles were smaller near the walls and reached their maximum at R/2. The bubble size increased with carboxymethylcellulose concentration and the superficial gas velocity. (University of Rhode Island)

Supercritical methanol is miscible with 1-methylnaphthalene in all proportions at 250°C to 300°C and pressures below 2,000 psia. The observation is relevant to the use of supercritical methanol for extracting coal because 1-methylnaphthalene is a product of coal pyrolysis. The solubilities of other coal-derived compounds in

supercritical methanol are being determined. (University of Delaware)

Collision-induced light scattering spectra of supercritical methane in the temperature range of 25°C to 80°C and density range of 180 to 500 amagat were examined. The spectra have two regions, arising from two different mechanisms: a low frequency region due to the dipole induced dipole (DID) mechanism, and a high frequency region due to the collision-induced rotational Raman (CIRR) effect. The two regions are characterized by different decay constants, which were computed. (University of Illinois, Urbana)

Catalysis and Kinetics

H.R. Appell, Coordinator

The objectives of this category 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 coal liquefaction studies in support of potential larger-scale processes.

Catalytic coal liquefaction studies applying the principles of "Hard-Soft" acids and bases (HSAB) were concluded and a revised mechanism was presented, consistent with both HASB theory and the experimental results. In essence, the theoretical picture consists of the Lewis Acid coordinating with a molecule of water in the first step, forming a Bronsted Acid, the active catalytic species. The proton of the Bronsted Acid then coordinates with an ether-oxygen in the coal molecule with a resultant weakening and then cleavage of the ether bond. The reason that the acids in the intermediate or borderline category are most effective is that these acids are strong enough to cause ether bond cleavage (the major bond cleavage at sub-softening conditions) but not strong enough to promote charring and other undesirable side reactions. The very soft acids usually have inadequate catalytic strength to promote the needed bond weakening for hydrogenolysis to occur. (University of Utah)

High-surface-area (40 m²/g) unsupported molybdenum sulfide was prepared by the flash decomposition of ammonium thiomolybdate in flowing helium. This molybdenum sulfide is being used in a basic study, which is free of support-induced complications, of the oxygen chemisorption on both supported and unsupported molybdenum

sulfide catalysts, of the nature of the active sites, and of the effect of the pretreatment on chemisorption behavior. This work involves temperature-programmed surface reduction, in which hydrogen chemisorbed at 20°C is removed as hydrogen sulfide on programmed heating in helium, then reduction in hydrogen followed by sulfiding in hydrogen sulfide, and then desorption of the hydrogen sulfide. The effect of these treatments will be correlated with the behavior of the catalyst as measured by its activity in the dehydrogenation of cyclohexane and the desulfurization of thiophene. In the preparation of the molybdenum sulfide, the highest surface areas were obtained at high heating rates. A higher surface area was obtained at 500°C than at 400°C. (SUNY at Buffalo)

The pyrolysis of several model compounds, including 9-benzyl-1,2,3,4-tetrahydrocarbazole and 1-benzyl-1,2,3,4-tetrahydroisoquinoline, is under investigation in order to learn how these molecules rupture and if the resulting fragments are stabilized by hydrogen available in these molecules and if the stabilization is intra- or intermolecular. Kinetic studies indicate that in the liquid phase, i.e., at temperatures of 315°C or less, the pyrolysis mechanism follows second-order kinetics. At temperatures of 365°C and above, where the model compounds were predominantly in the vapor phase, the pyrolysis mechanism follows first-order kinetics. Equilibrium studies of the decomposition of 9-benzyl-1,2,3,4-tetrahydrocarbazole show that at 375°C, almost complete conversion of this compound is favored thermodynamically; kinetic factors are therefore controlling the pyrolysis. (University of Utah)

Studies to evaluate catalytic functionalities of a CoMo/Al₂O₃ over feedstocks containing naphthalene, dibenzothiophene, dibenzofuran, and indole in binary mixtures showed significant differences in the interactions and effects of the reactants on their conversion rates. The data are in general agreement with the expected effect of the relative strengths of adsorption of the reactants on the catalyst surface. Model compounds decreased catalyst reactivity in the following order: N-compound > S-compound > O-compound > aromatic hydrocarbon. These results show that model compound studies conducted in the absence of other compounds, especially heterocyclics, do not adequately evaluate the various catalytic functionalities on sulfided hydrotreating catalysts. (University of Utah)

Studies of carbon formation on hydrotreating catalyst have been initiated with the objective of

understanding and utilizing the observation that the addition of titanocene dichloride to Solvent-Refined Coal reduces the extent of carbon formation during upgrading. Two reactors, one gradientless and the other a trickle bed, will be used in this investigation in order to pursue the problem from two viewpoints. Two different types of feedstocks, one a low carbon former and the other a high carbon former, will be used to determine the influence of the carbon-forming species on the mechanism of coke inhibition. (Oklahoma State University)

Tin chloride catalysts containing 1% to 4% tin were prepared by impregnation of silica, alumina, and silica-alumina with stannous chloride. Stannous oxide catalysts were prepared by treatment of the stannous chloride catalysts with ammonium hydroxide. Activities of these catalysts were determined by measuring the rates of hydrogenation of quinoline at temperatures of 200°C to 350°C and at pressures of 500 to 3500 psig. Hydrogenation followed pseudo-first-order kinetics, with the rate increasing linearly with tin content. The apparent activation energies for the SnCl/SiO₂ and the SnCl₂/SiO₂-Al₂O₃ catalysts were 15 and 18 kcal/mole, respectively. The plot of activity with catalyst loading with the silica-alumina supported catalyst did not pass through the origin, suggesting that the support itself showed significant catalytic activity for the hydrogenation of quinoline. (Western Kentucky University)

The coking tendency of n-hexadecane, tetralin, and mixtures of tetralin with anthracene, phenanthrene, and 1-methylnaphthalene was examined by boiling the hydrocarbon with Shell 324 catalysts (1/16-inch and 1/32-inch extrudates) for two hours at 207°C and atmospheric pressure. Coke formation varied with the hydrocarbons and the catalysts. Addition of titanocene dichloride appeared to increase the coke formation in several experiments. The coking tendency of the hydrocarbon under hydrotreatment conditions will be examined in the next quarter. (Oklahoma State University)

The activities of CoMo, CoCr, and NiCr catalysts for hydrogenation and CN hydrogenolysis were tested in a flow reactor at 277°C and 35 atmospheres. Although the activity of the Cr catalysts was appreciably lower than the activity of the Mo catalyst for both the hydrogenation and the hydrogenolysis reaction, the hydrogenolysis selectivity of the Cr catalysts was about five times larger than that of the Mo catalyst. Since high CN hydrogenolysis selectivity is a desirable property in a catalyst for upgrading coal-derived liquids,

other Cr preparations will be tested that may have high hydrogenolysis activity in addition to high hydrogenolysis selectivity. (University of Utah)

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.

An extensive series of studies comparing the Fischer-Tropsch reaction in the presence of different slurry vehicles (octacosane and phenanthrene) is still being analyzed. Some of the early work was affected by small amounts of a sulfur compound in the phenanthrene used. These studies were subsequently repeated with a highly purified phenanthrene. The nature of the liquid clearly has an effect on the reaction that may be related at least in part to the increased solubility of H₂ and CO in phenanthrene. (Massachusetts Institute of Technology)

The infrared spectrum of the Al₂O₃ - supported surface species Rh^I(CO)₂ has been measured for systematic isotopic substitution of CO¹⁸ for CO¹⁶. Six infrared bands are observed for the three possible isotopic species, confirming that the species is Rh^I(CO)₂ (C_{2v}). Force constants for the C-O stretching motion and for CO-CO interaction between the two CO ligands on Rh^I(CO)₂ have been evaluated and used to predict the spectrum of Rh^I(CO¹⁶)(CO¹⁸), which is in good accord with the experimental observations. Kinetic and infrared intensity measurements of the exchange process at 200°K indicate that the exchange occurs under nonequilibrium conditions, caused most likely by the participation of a slow CO diffusion process that is rate-controlling. (University of Pittsburgh)

The effect of the carbon monoxide and the hydrogen partial pressure on the behavior of a coprecipitated Fe-Mn catalyst (11.8 Mn/100 Fe) was determined at a temperature of 225°C and a space velocity of 1.33 cm³g⁻¹sec⁻¹. The catalyst was reduced with H₂ at 400°C for 8 hours and then

conditioned with 2:1 synthesis gas for an additional 12 hours prior to the testing periods. As the hydrogen partial pressure increased from 106 to 119 psia, the conversion of the CO increased from 2.0% to 9.3%, and the O/P ratio and the CO₂ production decreased, the methane increased, and the C₂-C₄, C₅⁺, and ROH content remained unchanged. Increasing the CO partial pressure while holding the hydrogen partial pressure constant generally opposed the results of increasing the hydrogen partial pressure except that the C₅⁺ content increased instead of remaining constant. (University of Utah)

Bifunctional catalysts consisting of palladium or platinum supported on ZSM-5 were tested for synthesis gas conversion. A catalyst consisting of 1.8% Pt/ZSM-5 converted synthesis gas (H₂/CO = 1) at 350°C, 36 atm, and GHSV = 900 hr⁻¹ to a hydrocarbon product with a selectivity of 86% for the gasoline range (C₅-C₁₁), far exceeding the Schulz-Flory theoretical limit of 46%. The H₂ + CO was low (10%), possibly because of the low platinum content in the catalyst and the large ZSM-5 particle size (60 μ). The catalyst was prepared by a direct synthesis method in which platinum chloride was added to the synthesis mixture used in the preparation of ZSM-5. Efforts are being made to prepare Pt/ZSM-5 catalysts with other compositions and particle sizes in order to raise the synthesis gas conversion. (Worcester Polytechnic Institute)

With the objective of developing solid-state NMR techniques for characterizing zeolite catalysts, samples of high purity ¹⁷O-enriched Na-Y faujasite were prepared and characterized by ²⁷Al and ²⁹Si magic angle sample spinning nuclear magnetic resonance (MASSNMR). The ²⁷Al spectra showed only one line, arising from tetrahedrally coordinated Al, while the ²⁹Si spectra showed four lines, arising from Si atoms coordinated to different numbers of Al. In the next quarter, ²⁷Al and ²⁹Si spectra by variable angle sample spinning nuclear magnetic resonance (VASSNMR) will be investigated, and ¹⁷O spectra by both MASSNMR and VASSNMR will be investigated. (University of Pittsburgh)

Structure and Characteristics of Coal *S. Friedman, Coordinator*

The objectives are to study the chemical structure of coal and products derived from coal by extraction or liquefaction, using chemical and physicochemical methods, to identify those fea-

tures of coal that have significance to coal conversion and utilization.

The absolute sensitivity of the new laser-induced coal fluorescence technique for determining fluorescence decay times was about 0.1 ns. Subsequent measurements on coal macerals indicated a trend toward decreasing decay times with an increase in emitted peak wavelength. (Southern Illinois University)

Coal samples chosen specifically for their proximity to the Appalachian folding belt in eastern West Virginia and Alabama, where the potential effect of stresses is high, have been examined for anisotropic nature and its relative magnitude. For coals of similar rank, weakly anisotropic samples produce more volatile material than those having strong anisotropy when subjected to pyrolysis gas chromatography. (West Virginia University)

Forty-three coal samples, most of them from Western Kentucky, have been examined using quantitative fluorescence microscopy of sporinite to determine if rank as determined by vitrinite reflectance could be correlated with selected fluorescence parameters. All eight parameters (highest intensity wavelength; area under peak to left of peak; areas in the blue, green, yellow, and red wavelengths; blue-red and red-green ratios) correlated with coal rank. The red and yellow were the best predictor variables of rank. The individual parameters of red area and blue-red ratio accounted for the greatest variance in predicting coal rank. (University of Kentucky)

A number of superatmospheric pressure measurements of isothermal fluidity of coal in a high-pressure Gieseler plastometer have been completed. The THF extracts of the 40 coals used in this study have been characterized by HPLC; and the coals, the extraction residues, and selected THF extracts have been examined by FTIR. These data are being used to derive a statistical approach to predicting plasticity in bituminous coal. (Western Kentucky University)

Measurements of aliphatic C-H content by FTIR have been correlated to the plastic properties and liquefaction behavior of a set of coals and vitrinite concentrates obtained from the Kittanning seam. The total aliphatic C-H content of the vitrinite concentrates correlates with Gieseler fluidity, which displays an abrupt change over a narrow range of aliphatic C-H content. Liquefaction conversion does not correlate with FTIR measurements of total aliphatic C-H content but does correlate with the intensity of a CH₂ band. These results confirm the general relationship between the mechanism

of liquefaction conversion and plastic development, but also suggest some subtle differences. (Pennsylvania State University)

An inventory of the Penn State Sample Bank has been completed and provides information on the quantity and quality of all samples contained in the Bank. Software has been completed that permits the use and daily updating of the computerized inventory as a part of the routine operation of the Sample Bank, as well as the recording, tabulating, and summarizing of information on the requests for coal samples received from DOE contractors and others. At a meeting of Penn State personnel and personnel from DOE (from Washington and Pittsburgh), a series of 65 coals was examined for consideration in the DOE Sample Suite. (Pennsylvania State University)

Work has begun on a three-part study to produce superclean coal using the microbubble flotation procedure. With this technique, air bubbles of less than 80 microns in diameter are used to float finely pulverized coal particles. The three-phased approach will examine the fundamentals of fine particle flotation, bench-scale studies, and continuous column flotation experiments. (Virginia Polytechnic Institute)

Characteristics and Analyses of Coal-Derived Liquids *L. Makovsky, Coordinator*

The objectives are to develop instrumental techniques that will help elucidate the structures present in complex coal molecules and the products of coal conversion processes.

Analyses were undertaken of three aqueous liquefaction specimens: a Disposable Catalyst Development (DCD) process effluent from Pittsburgh, Pa., and two effluents generated by three separate process units from Wilsonville, Ala. The Wilsonville effluents resulted from sampling at different wastewater treatment steps. Thiosulfate and sulfate were observed in the Wilsonville effluents. The DCD process effluent contained only hydrogen sulfide and polysulfides. (Pennsylvania State University)

The vapor-liquid-equilibrium data of light gases in hydrogen/coal liquid model compound systems were obtained, yielding infinite dilution K values that were converted when possible to Henry's constants. Attempts are being made to develop a generalized correlation for predicting vapor pressures of coal liquid compounds and regular hydrocarbon series. (Rice University)

Some probable structures have been assigned to the three bands in the 900-700 cm^{-1} spectrum of coal after applying Fourier self-deconvolution (FSD). The 800 cm^{-1} band may be assigned to a ring with isolated C-H groups, i.e., both neighboring carbon atoms are substituted. The 820 cm^{-1} and 760 cm^{-1} bands are due to two and four neighboring C-H groups, respectively. Also, it is believed that the lower wave-number component of each band doublet observed after FSD is due to contributions from mononuclear rings, whereas the higher wave-number component is assignable to polynuclear rings. (University of California, Riverside)

Research continued on applying laser desorption mass spectrometry (LDMS) to the analysis of coal. A known polymeric material, paralene, was analyzed by LDMS. The results showed enhancement of the higher molecular weight homologs by the LDMS method. Also, initial work has begun on characterizing two different chemically degraded coal samples: an acidified fraction of ruthenium tetroxide oxidation of an Illinois No. 2 coal, and the THF-soluble fraction of an electron-transfer reduction of an Illinois No. 6 coal using a crown ether for the phase-transfer catalyst. (Purdue University)

On-line FTIR spectroscopy detection has been combined with HPLC in the normal phase mode for the analysis of azaarenes and aromatic amines in coal-derived products. Model compound mixtures were used to establish conditions for elution of a coal-derived sample from a bonded-phase amino column with a mobile phase of 70:30 of $\text{CDCl}_3:\text{CCl}_4$ + 0.02% triethylamine. Basic nitrogen components in the THF solubles from liquefaction of Wyodak No. 3 in 1,2,3,4-tetrahydroquinoline were investigated. It was shown that these basic-nitrogen compounds can be chromatographed on a system amenable to IR detection that can provide structural information not available from typical LC detectors. (Virginia Polytechnic Institute and State University)

The behavior of narrow molecular weight ranges of lignite-derived asphaltenes and pre-asphaltenes was compared with model oligomers of several types by high pressure gel permeation. Based on vapor pressure osmometry (VPO) molecular weights in the range of 2000-3000 Daltons, the lignite-derived fractions fit the same calibration plot as polystyrene and aryl-ether oligomers. Asphaltenes with a high degree of aromatic condensation, particularly at low molecular weights, behaved in a manner similar to models

with condensed aryl systems, i.e., the retention volumes were too large. Low molecular weight hydroxyl-containing oligomers gave too small a retention volume, indicating hydrogen-bonding with the solvent. (The University of North Dakota)

Phase Equilibrium Properties of Coal-Derived Liquids

A new flask equilibrium cell capable of maintaining a seal between the cell and the sight window over many temperature cycles was designed, constructed, and tested. The final design employed a custom sapphire window with gold O-rings for the seals.

Studies are now in progress on the phase behavior of the m-cresol-quinoline binary systems. The m-cresol-quinoline binary system was selected because its phase behavior is typical of the hetero-atomic species present in coal-derived liquids, and the system is expected to be highly non-ideal. Initial data obtained have been compared to data generated with a modified Soave-Redlich-Kwong equation with interaction parameters found by use of experimental data. These data were close to the predicted values. The values of the interaction constants were $C_{12} = -0.075$ and $D_{12} = 0.005$. The negative value of C_{12} is indicative of a negative departure from Raoult's Law, as would be expected for association between two compounds of a mixture. Correlations have been limited to those that predict simple polar fluids. (Colorado School of Mines)

Enthalpy Measurements of Coal-Derived Liquids

The final report was prepared and issued for the contract. This report summarizes the results of the last 30 months of effort in two main areas of research: experimental measurement of enthalpies for quinoline using a Freon boil-off flow calorimeter, and an investigation of the applicability of cubic equations of state to correlating the enthalpy of coal-liquids.

In the first part of the report, the compound quinoline is discussed. Process flow in the flow calorimeter, operational problems, and equipment modifications are described. Procedural modifications, including a new sample purification procedure, are described.

Quinoline enthalpy data are presented along the isobars of 517.1, 689.5, 1034.2, 1379, 3799.1, and 10342.5 kPa over a temperature range of 340K to 664K.

Experimental enthalpy values and thermodynamic properties derived from this data are

compared to corresponding values in the literature and to values predicted using computer-aided calculations involving three correlations. The three correlations are the SRK equation of state and two modifications of the BWR equation of state by Kesler et al. and Starling, respectively. In general, the correlations do not accurately predict the thermodynamic behavior of quinoline. However, the experimental data compare well with available literature data for quinoline vapor pressures.

The second part of the report discusses the correlational effort. This includes a discussion of past correlational work and the difficulties associated with a general correlation for coal liquid enthalpy. In addition, experimental data and computer-generated predictions are presented.

Previous work has shown that any correlation will require the inclusion of a parameter measuring the association effects inherent in most organic systems. Cryoscopic molecular weight determinations using the freezing point depression method as a means of measuring degree of association were done for several systems. Data and molecular weight versus solute/solvent concentration curves are presented for ethanol, n-butanol, n-pentanol, n-hexanol, m-cresol, quinoline, and five quinoline/m-cresol mixtures (20, 33, 50, 66, 80 mol% m-cresol). The first five systems exhibited a high degree of association due to hydrogen bonding caused by the hydroxyl groups. Quinoline, as expected, evinced little variation in molecular weight with concentration and thus has little or no association occurring. The five quinoline/m-cresol mixtures exhibited unusual nonlinear behavior, which may be due to acid-base chemical interactions.

The remainder of the research involved analyzing the capabilities of cubic equations of state with regard to the problem of a coal-liquid enthalpy correlation. This includes a comparison of correlational methods and a discussion of the theory and application of cubic equations. Three cubic equations of state were chosen as representatives of this class. They were the Soave equation, the Peng-Robinson equation, and the Modified Soave equation. The first two equations are three-parameter models, and the last equation is a four-parameter extension of the SRK equation capable of modeling polar systems.

The three equations were used to predict vapor pressures and enthalpies for ten pure component systems previously studied in the lab: benzene, m-cresol, transdecalin, n-hexanol, lutidine, 1-methylnaphthalene, n-pentanol, quinoline, thio-

phene, and m-xylene. Also, the equations were used to predict the heat of mixing at 298K and liquid enthalpy departures at high pressures and temperatures for the quinoline/m-cresol mixture system. Data, predictions, and comparisons are all presented.

In general, the results were encouraging. All three equations were effective in predicting both enthalpies and vapor pressures. In addition, the equations worked well when fit to mixture enthalpies. Peng-Robinson and SRK were essentially equal in their ability to model enthalpies, although the equations consistently predicted low, particularly for systems with association. The Modified SRK equation was superior to the other equations and modeled all properties for both associating and non-associating systems well. The Modified SRK equation did have a drawback in that it was not readily generalized because it required two parameters that must be fit to data for best results. In sum, it was shown that a four-parameter equation of state could be used successfully to correlate the enthalpy of coal-liquid model compounds. (Colorado School of Mines)

Twenty-one samples of Kentucky coals were analyzed for inorganic oxygen and silicon, and the following correlation was established:

$$\text{Inorganic oxygen} = (3.95 + 0.93) + (1.83 \pm 0.13) \times \text{silicon}$$

The ash content of these coals varied from 2.12% to 53.0%, and the silicon content from 0.54% to 12.7%. The applicability of the correlation to coals of different ranks from various parts of this country has not yet been established. (University of Kentucky)

A mixture of 70 mol% tetralin and 30 mol% phenol gave a vapor pressure of 32 psia at 227°C. However, when 50 wt% of coal-derived solids from SRC II was added to the mixture, the vapor pressure went up to 40 psia. It appears that the solids adsorbed the less volatile component of the mixture preferentially, whereby the concentration of the more volatile component in the liquid phase and the vapor pressure increased. The effect of coal solids on the vapor pressure of coal liquids is being investigated in view of its importance in the distillation of the products of coal liquefaction. (University of Pittsburgh)

Gum in coal-derived distillate fuels may be removed by treatment with small quantities of pentane, hexane, or heptane. Samples of 450°C to 650°F and 650°F- endpoint distillates from the

Wilsonville plant were treated with pentane, hexane, and heptane, and the mixtures stirred overnight at room temperature. The separated gum was found sticking to the walls of the glass vessel. (Northeastern University)

Gasification

J.C. Winslow, Coordinator

The objective is to develop new concepts and improve the existing technology for gasification of coal.

An experimental apparatus is now being used to perform simulations and measurements for the diffusion of gases in porous solids. The viscosity of argon, nitrogen, and carbon dioxide, and also the diffusivity of argon-carbon dioxide and nitrogen-carbon dioxide gas pairs have been measured over a range of elevated temperatures. (University of California)

The study of potassium carbonate catalyzed gasification of coal has produced several conclusive results: (1) temperature-programmed reaction (TPR) appears to be a powerful technique for studying alkali metal catalysis of carbon gasification; (2) carbon reduces potassium carbonate at temperatures as low as 550°K; (3) the carbonate ions of the complex are bound to the surface in two distinct states; and (4) elemental potassium undergoes a two-step oxidation-reduction cycle, which is responsible for the catalytic gasification of carbon by CO₂. These and other findings have recently been published in a master's degree thesis. (University of Colorado)

Combustion

J.C. Winslow, Coordinator

The objective is to study fundamental aspects of coal combustion and combustion of coal oil slurry of coal-derived liquids that may lead to improvements in coal utilization.

The Computer-aided Particle Tracking Facility at the University of Illinois has been used to obtain mean velocity distributions of the solid particles in a gas fluidized bed, with and without simulated heat exchange tube banks. The recirculation patterns of the solid particles are only moderately affected by the presence of the tube banks, but the magnitudes of the recirculation velocities are reduced drastically. The results provide a quantitative assessment of the role of internals on solids' motion that was hitherto not available in the literature. (University of Illinois)

Two ash deposit samples from the Purdue University power plant were studied in packed beds in a newly completed High Temperature Test Facility. The surface temperatures of the packed beds were as high as 1381°C. Sintering began at about 985°C and melting at approximately 1280°C. Overall thermal conductances varied from 0.15W/m.k at 300°C mean ash temperature to as high as 0.46W/m.k at 1150°C ash temperature. Local values of thermal conductance at various bed levels were also measured during heating and cooling of the packed beds. (Purdue University)

An experimental system has been constructed and some preliminary data have been obtained for an investigation of the thermal decomposition of pulverized coal in hot flue gas environments. The experiments indicate that the laminar pulverized-coal opposed-jet-combustion configuration is a novel tool that permits quantitative studies to be performed at high heating rates and temperatures in excess of 1500K. Theoretical work has shown that the configuration is one-dimensional in concentrations, temperature, particle density, and particle temperature; and it can be modeled to whatever complexity is appropriate. (University of Arizona)

The fluxes of descending large particles and agglomerates were measured at heights from 0.7 to 1.9 m above a bed of particles having solid density and mean size similar to those present in the MIT Atmospheric-Pressure Fluidized-Bed Combustor. The particle flux decreased approximately exponentially with height in this region. The characteristic lengths for decay of the descending particle flux were similar in magnitude to those reported previously for the decay of ascending particle flux above beds of smaller particles of various materials. The dependence of this characteristic length on superficial velocity has not usually been well established in studies of ascending particle flux over limited ranges of superficial velocity. The characteristic lengths determined in the present investigation were approximately proportional to superficial velocity, in agreement with the observations of Lewis. (Massachusetts Institute of Technology)

The study of the oxidation of HCN using an atmospheric-pressure flow system with a plug flow reactor was continued. Attempts to find conditions at which NO formation from the oxidation of HCN-fuel additive mixtures was in its initial stages were again unsuccessful. Nine samples of white solid product formed from HCN oxidation at flameless conditions (negligible NO yields) were collected and examined. From infrared and ele-

mental analyses and physical characteristics, it appeared that the product was ammonium cyanate at low extents of reaction and when CO was the additive. However, when hydrogen was the additive and at higher extents of reaction, the product appeared similar to urea. (Western Michigan University)

In the freeboard region of fluidized bed combustors (FBC), the tube surface is exposed alternately to a dense-emulsion phase and to a lean-void phase. The average heat transfer coefficient at the solid surface is then the weighted average. The dynamic parameters for this phenomenon are being completed from the capacitance probe data obtained previously. In addition, the development of a phenomenological model and a correlation for the heat transfer process for horizontal tubes in the freeboard region of FBC's are in progress. (Lehigh University)

Environment

J.C. Winslow, Coordinator

The objectives are to develop techniques to identify and resolve environmental pollution problems associated with coal conversion and utilization.

Laboratory evaluation of a new process configuration for the treatment of liquid effluents from coal conversion processes has been completed. The wastewater treatment process studied consists of a contact-stabilization activated-sludge system with powdered activated-carbon addition, followed by activated-sludge nitrification and denitrification in an anoxic filter. Three experimental reactor systems were operated at average powdered activated-carbon (PAC) concentrations of 0 mg/L, 980 mg/L, and 1960 mg/L. Different contact-stabilization solids retention times were then evaluated at these PAC concentrations during three phases of operation. Contact tank hydraulic detention times were subsequently varied while maintaining a solids retention time of 30 days. (University of Illinois)

In an effort to examine the pollutants from various coal conversion processes, work concentrated on studying the products formed during coal pyrolysis. Flash pyrolysis data of New Mexico subbituminous coal in a laminar flow reactor exhibit a distinct pattern of devolatilization. At temperatures less than 400°C, little or no devolatilization occurred; only moisture in the coal feedstock volatilized. Between 500°C and 900°C, the major fraction of volatile matter was released. Increases in temperature above 900°C produce

small increases in asymptotic weight loss. Plots of asymptotic weight loss from other studies fall very close to a single curve over a temperature range of 400°C to 1000°C. Weight loss data from this study fall along the same curve. (North Carolina State University)

Pulverized Coal Combustion

J.D. Hickerson, Coordinator

The objective of this project is the development of a technology base to support expanded utilization of coal and coal-based fuels.

A workshop on the "Behavior of Coal Mineral Matter/Ash in Combustion Systems" was held in Pittsburgh during the period December 6-7, 1983. Thirty-five prominent scientists representing industry, commercial research companies, universities, national laboratories, EPRI, UNDERC, and PETC contributed to this effort. The workshop divided the problem of slagging in coal-fired boilers into tractable segments that could be analyzed in a two-day period:

- Characterization of Minerals and Deposits
 - Evolution and Transformation of Mineral Species in Flames
 - Mechanisms of Mineral Species Transport
 - Initiation, Growth, and Aging of Deposits
 - Effects of Ash on Thermal Performance

Each workshop division made recommendations on research needs that would lead to methods of overcoming ash-related problems in coal-burning combustors. These recommendations are now under study, with the immediate objective of developing an effective integrated AR&TD Direct Utilization Program; this program will deal with the problem of slagging, where the benefits derived will have a shorter time route to the point of need, the combustor. (PETC, DU-AR&TD)

Investigators have characterized a barrel of Pittsburgh Seam coal by several methods. Sedimentation behavior in CWM suspensions as a function of coal concentration suggests that particle-particle repulsion can lead to an ordering of the coal particles. This ordering may result in a configuration that both maximizes particle-particle distances and provides more efficient packing. This phenomenon may explain sedimentation behavior and might be used in the optimization of coal/water slurry properties.

Rheology of Slurries with Additives

Pittsburgh No. 8 was studied with the following additives: Aerosol OT (anionic), sodium dodecyl sulfate (SDS, anionic), cetyl trimethylammonium bromide (CTAB, cationic), Triton X-100 (non-ionic). In the coal concentration range 50 wt% to 70 wt%, the effect of increasing additive concentration on viscosity is as shown in Table 6.

For coal concentrations ≥ 60 wt%, the slurries exhibit a yield stress, which with increasing concentration of additive is as shown in Table 7. The slurries are Bingham plastic at the higher coal concentrations, while at < 60 wt% most are either pseudoplastic or approximately Newtonian, depending on additive type and concentration. Some slurries are dilatant.

Of the four agents tested, the non-ionic Triton X-100 is the most effective at reducing viscosity and yield stress, at both the acidic natural pH and at pH 7. Changes on standing for one week are not significant.

Electrophoresis of Slurries with Additives

The electrophoretic mobility has been measured for 50 wt% Pittsburgh No. 8 slurries in solution with SDS, CTAB, and Triton X-100 at the natural pH and pH 7. Mobility data are difficult to explain in terms of simple charge considerations. Charge reversals were observed under conditions where they would not be predicted; these findings

Table 6.
Viscosity, Increasing Additive Concentration
(50 wt% to 70 wt% coal)

	Aerosol OT Anionic	SDS Anionic	CTAB Cationic	Triton Non-ionic
Natural pH (~ 3.8)	increase	decrease	decrease	decrease
pH 7	decrease	decrease	increase	decrease

Table 7.
Yield Stress, Increasing Additive Concentration
(≥ 60 wt% coal)

	Aerosol OT Anionic	SDS Anionic	CATB Cationic	Triton Non-Ionic
Natural pH (~ 3.8)	increases	decreases	decreases	decreases
pH 7	increases	decreases	increases	decreases

were considered to be related to surface contaminants. In some cases, good correlations between electrophoretic mobility and rheology data were found.

Sedimentation of Slurries with Additives

Slurries with 25 wt% of Illinois No. 6 and of Hiawatha coals at both the acidic natural pH and at pH ~ 7 , and of San Juan coal at its natural pH of 6.8, were prepared in solutions of Aerosol OT, SDS, CTAB, and Triton X-100 up to 0.36 wt%. The sedimentation rate and final settled volumes were measured for both the initial suspension and for resuspension after two weeks. Similar experiments using Pittsburgh No. 8 with the four additives, started during the previous quarter, were also completed. Some patterns are beginning to become apparent. For instance, Aerosol OT interacted strongly with the two most hydrophobic coals, Pittsburgh No. 8 and Hiawatha, presumably through hydrophobic adsorption and bridging of particles. Electrostatic interactions occurred between coal particles and ionic surfactants with head groups of opposite charge, as observed especially with San Juan and Hiawatha, the more strongly negatively charged coals, in CTAB, the cationic surfactant. In surfactants other than Aerosol OT, Pittsburgh and Hiawatha coals tended to have no mass subsidence when there was no opportunity for electrostatic interaction, while Illinois No. 6 and San Juan did not show this behavior. The results of wettability and sedimentation experiments were in qualitative agreement, and for Pittsburgh No. 8, the sedimentation experiments could be correlated to the electrophoretic mobility and rheology measurements in most cases. However, complete interpretation of sedimentation results must wait for completion of electrophoretic mobility measurements on the three remaining coals in the various surfactants, and for the completion of surface tension measurements on the supernatants of the sedimentation samples.

Surface Tension Measurements in Coal-Water Slurries

The amount of surfactant adsorbed on coal particles is being estimated by measurements of the surface tension of the supernatant after sedimentation, but results are not far enough along to be reported.

Overall, although the interactions among coal, liquid, and additive are complex, time-dependent, and difficult to interpret, a pattern of interrelationships is emerging. It is expected that a preliminary model for the effects of additives can be developed when the experiments now under way are completed.

CWM Atomization Theory

A computer code was developed to solve the system of equations for a slurry jet (consisting of solid particles and liquid droplets) penetrating quiescent air. The model originally developed by J.K. Dukowicz, applicable to liquid sprays, has been the basis of this development. The coupling between gas and particles is through the void fraction (fraction of volume occupied by the gas), and the momentum interchange between particles and gas. The spray entering the computational domain is assumed to consist of a discrete number of particles, and a statistical approach is employed to formulate the particle-size distribution (as developed by Cloutman et al.). The spray is also assumed to be non-evaporating. The particle size is a constant throughout the calculation. The initial conditions for the particles are assumed to a known initial particle size and velocity distribution. The two sets of equations, one set for the gas phase and one for the liquid/solid phase, are solved for a Eulerian gas and Lagrangian particles. The formulation is transient and two dimensional in space for a axisymmetric geometry. A time-marching finite difference technique is employed, which is partially implicit. Particle/droplet interactions are considered, and

elastic collision is described in the model. (Carnegie-Mellon University)

Investigators have been studying the basic combustion and pollutant formation processes for pulverized fuels. Principal objectives were the measurement of local product composition and pollutant formation for coal-water mixtures (CWM), the measurement of the physical and combustion characteristics of several different coal-derived chars, and the implementation of swirling flow and heterogeneous char reactions in a two-dimensional predictive coal combustion code (PCGC-2).

Additional objectives included (1) a parametric study of the effect of operating variables on CWM combustion and (2) char combustion tests to supplement reactivity and physical property measurements. Contacts with industrial and governmental organizations were continued, and reports and papers were published in order to transfer information to the technical community.

Coal-Water Mixtures

Coal-water mixture (CWM) combustion mapping tests were conducted in a laboratory reactor to identify space-resolved coal burnout, gaseous and solid products composition, and ash and particle flux and fluid temperature. Slurry reaction processes were studied, and a data base with known boundary conditions was developed for use in predictive and interpretive codes. The reactor operating conditions for the tests, which utilized a state-of-the-art, commercially available slurry, were determined from a parametric characterization study to optimize coal burnout and were similar to industrial furnace settings for pulverized coal. The CWM combustor was designed and built to obtain local combustion samples, with control of combustion air temperature, swirl and flow rates, atomizing air flow rate, and slurry spray pattern and flow rate. The reactor was designed for control of wall temperature, with computer interface for automatic operation and data acquisition.

Coal burnout of 98% was achieved at 15% excess air and a secondary inlet swirl number of 1.5 with a stable flame and no support fuel. It was observed that burnout had reached near-maximum values by approximately half-way through the reactor. The composition of the products also changed only slightly from the midsection of the reactor to the exit. From ash and particle flux measurements, it was determined that vigorous mixing of the slurry and preheated air took place due to the spray pattern and particle momentum,

which contributed to the relatively high coal burnout with particle residence times less than 100 msec. Even with high burnout, large agglomerates were found in combustion samples removed near the reactor exit.

Gaseous combustion products contained very low carbon monoxide concentrations, while NO_x levels were similar to those in combustion experiments with pulverized coal using a single-stage burner. A slight increase in NO_x along the length of the reactor was observed for given operating conditions. Sulfur emissions were detected only in the form of SO_2 , indicating that no fuel-rich regions existed in the reactor that could produce other sulfur compounds with carbon and hydrogen. This finding was consistent with the high mixing rates in the combustor.

Char Characterization

The chars used in the study, obtained from the variety of parent processes, exhibited a wide variety of characteristics. The chars were received from Bi-Gas (BGM and BGP), F.M.C. (FMC), Occidental (OLS and OPP), Rockwell (RHD, RHL60, and RHL600) and Toscoal (TBS). As-received size varied from a mass mean diameter of 1000 μm for TBS to 60 μm for OPP. Proximate analysis showed the volatile content varying from 17.0% for TBS and 15.1% for OLS to 3.5% for BGP. The BET measurements divided the chars into those with quite high surface areas (BGM, BGP, OLS, OPP), those with low surface areas (RHD, RHL60, RHL600), and TBS and FMC in between. Density measurements identified those with high porosity and low bulk density (BGM, OLS, RHG) and those with low porosity and high bulk density (FMC, TBS). Scanning electron micrographs were used to visually classify the chars; similarities were observed in BGM, OLS, and RHG. Elemental analysis of the chars showed all the chars to be high in carbon and ash, and low in hydrogen, nitrogen, sulfur, and oxygen. The only exceptions were the oxygen levels of OLS and TBS. After size reduction, the particle size distributions were similar for ash chars.

Reactivity tests were conducted in three temperature zones to correlate physical properties, char formation process, and reactivity in each temperature zone. All of the reactivity tests showed OLS to be the most reactive of the chars. The BGM was almost as reactive as OLS in zone II (intermediate temperature) tests by Phillips Petroleum Co. but was considerably less reactive in low temperature (zone I) TGA tests at Penn State. The TBS was quite unreactive in zone II but

was second most reactive in the RGA analysis. Other chars also exhibited relative changes in reactivity as test conditions were varied. In the high temperature (zone III) drop-tube furnace tests, the chars were much closer in reactivity than in either the Phillips Petroleum zone II tests, where two orders of magnitude separated the most reactive from the least reactive, or the Penn State TGA tests.

Laboratory-scale combustion tests were conducted with two of the study chars. The char volatile content had a significant effect on flame stability. The OPP and the TBS exhibited the most stable flames. The TBS had a higher volatile content than OPP, but the OPP flame was attached under all conditions, while the TBS did not burn with an attached flame. Burnout did not seem to be related to volatile contents or flame stability, since all chars exhibited high burnouts under certain conditions. Reactor-operating factors, such as temperature and residence time, had a strong influence on burnout.

Modeling of Char Combustion and Swirl

A general heterogeneous char reaction model was developed for application to various kinetic systems and pore evolutionary patterns. The pore model developed by Gavalas was amenable to studies where the pore size distribution could be changed for a given porosity. The Amundson pore model was judged to be geared more toward studies that exhibit difference in surface-area-burnoff characteristics. The utility of this char model lies in the potential parametric studies to which it is easily adaptable, in the exploration of test conditions, or in the analysis of experimental burnout or reactivity data.

Implementation of swirling-flow modifications into PCGC-2 was completed and evaluated with respect to the two-equation $k-\epsilon$ turbulence model. A summary and treatment of the PCGC-2 code, along with the swirling-flow incorporation, have been documented in a User's Manual. Both the code and the associated manual are now available for general use. The single particle char model is also available for interpretative purposes.

In addition to the final report, research results are documented in quarterly progress reports, one doctoral dissertation, five Master of Science theses, one Master of Engineering project report, two papers presented at coal slurry symposia, and two technical journal publications. Five technical presentations were also made at com-

bustion meetings. The Technical Advisory Committee, comprising twenty industrial and governmental representatives, met during the study period to review the results of this research program. (Brigham Young University)

Recent effort in coal combustion studies was focused on the effect of the particle-size distribution on the measured-temperature distribution and mass conversions. Even in a one-dimensional laminar flow field, particle temperatures and mass conversion for burning pulverized fuels are widely distributed because broad size distributions are unavoidable. For this study, number distributions of particle size, broadened by fine fragments generated as the particles are classified, span a range of at least one-hundred microns. Since the burning rate is sensitive to particle size, the temperature and mass conversion measurements reflect the size distribution as well as the kinetics of burning.

In order to characterize this effect, the governing mass, energy, and momentum conservation equations were solved subject to experimental conditions and to the assumption that diffusion-limited burning occurred for all particle sizes. Although this assumption may not be appropriate at these conditions, especially for the smaller sizes, this case illustrates the implicit coupling between particle size, temperature, and burning rate, which must always be recognized.

Table 8 shows temperature, particle size, and mass conversion as a function of the initial particle size at a height of 10 cm in the reactor. The initial particle-size distribution was somewhat narrow, with about 50% of the mass within 15 μm of the mass mean diameter of 90 μm . Particles at 300K were injected at the gas velocity of 165 cm/s into an environment at 1500K containing 10% oxygen. Constant density burning was assumed once they heated up to 1000K (about 15 ms for a 100- μm particle). At 10 cm into the reactor, particles having an initial-diameter below about 55 μm had completely burned out, and about 45% of the initial weight fed to the reactor had been lost. The mass mean particle size had been reduced to 87 μm , and the arithmetic mean temperature was 1898K. Note that although the fractional weight loss of the mean particle size fed to the reactor nearly reflects the overall fractional weight loss, the arithmetic mean temperature is not the temperature of the mean particle size.

The results clearly show that for polydispersed reacting particle streams, broad ranges of temperature and mass conversions will occur at any ax-

Table 8.
Particle Size, Temperature, and Mass Conversion
10 cm in the Laminar Flow Reactor: Constant Density Burning*

Initial Particle Diameter (μm)	Particle Temperature (K)	Particle Diameter (μm)	Percent Mass Loss
10	2115	0	99.9
20	2109	0	99.9
30	2104	0	99.9
40	2099	0	99.9
50	2094	0	99.9
60	2000	26.3	99.2
70	1936	45.9	71.9
80	1894	61.0	55.7
90	1860	74.5	43.3
100	1827	87.1	33.9
110	1791	99.2	26.7
120	1747	110.9	21.0
130	1692	122.4	16.6
140	1628	133.6	13.0
150	1554	144.8	10.1
160	1474	155.8	7.7
170	1389	166.7	5.8
180	1303	177.5	4.1
190	1216	188.3	2.7
200	1130	199.0	1.5

*Particle density = 1.0 g/cc

Gas Temperature = 1500K

Oxygen Partial Pressure = 0.10 atm

ial position of the laminar flow reactors. This fact may necessitate making simultaneous measurements of particle size and temperature when attempting to determine the kinetic parameters for the overall particle-burning rates. With the aid of the numerical model developed, however, it may be possible to deduce the kinetic parameters from measurements of the initial particle size distribution and the measured cumulative temperature distribution at successive heights of the reactor. This possibility is being investigated. The two-color temperature measurement technique is being modified to incorporate an optical particle sizer. The technique of interest is an imaging one, in which emission from the particle is recorded as it traverses a double-slit mask. An advantage of this technique is that particle velocities can be determined as well.

Details of the effect of the particle-size distribution on the measured temperature distribution

were presented at the 1983 International Conference on Coal Science, August 15-19, in Pittsburgh, Pa. (Sandia National Laboratory)

The extinction efficiency has been measured for five coals in a small-scale reactor. Results show scattering to be important and the extinction factor to be greater than 2.5. The extinction efficiencies were adequately predicted for most coals using Mie theory. Discrepancies observed were most apparent for anthracite, which had high unburnt carbon in the ash, and for the Four Corners coals, which, at a wavelength of 2.6 microns, exhibited non-gray behavior.

Heat transfer and extinction measurements were made for natural gas flames and for flames burning three different coals in a pilot-scale combustor. The extinction factors were similar to those measured in the small-scale reactor. As expected, high ash coals resulted in more deposition, radiation, and scattering. However, only

small differences were detected between the overall thermal performance of the gas and coal fuels (EER, Inc.)

Investigators have taken subbituminous and bituminous coal particles in a flowing stream of nitrogen and subjected them to rapid heating by a high power Carbon Dioxide Laser. Surprising results have been obtained through analysis of the particles that had been subjected to rapid heating and quenching. These are summarized as follows:

- Very little gas phase yield was detected from Wyoming and Montana Rosebud Subbituminous, and Pittsburgh No. 8 Bituminous coals under conditions of 10 to 30 msec heating at temperatures in excess of 1400K. Flame ionization detector chromatography indicated that less than 1% of the coal carbon is converted to gas-phase hydrocarbons.

- Proximate and ultimate analyses were consistent in that they clearly indicated little compositional change from the raw unheated coals, with the exception of moisture content.

- Visual inspection as well as electron microscopy clearly showed the effects of heating, with a fine-particulate phase being generated from the heating. Multiple blowholes were observed in the heated particles.

- FTIR analysis indicated no detectable change in chemical bond structure between heated and raw coals.

- Solubility of the heated samples is markedly enhanced as compared to raw coals. The extract consists of high molecular weight structures (up to 3000) as determined by gel permeation chromatographic analysis. The hydrogen content of the extract is significantly higher than that of the raw coals.

Clearly, the primary product of devolatilization at high heating rates is tars. It is hypothesized that previous observations of gas phase products are purely the consequence of secondary gas phase reactions or secondary decomposition of tar molecules in the hot gas background. This experiment by its very nature provides a rapid quench of the primary product stream, preventing occurrence of such reactions. (Avco, Everett)

Two classes of systems that can be used to study in detail the basic mechanisms that occur in the pyrolysis and combustion of pulverized coal were investigated. These systems included (1) laser-heated coal particles, particle arrays, and

coal sections, and (2) laminar coal dust-air flames. Techniques for the study of both of these classes of systems were developed and refined.

Among the single particle experiments, the technique in which individual particles are isolated in the interstices of grids and heated by IR laser radiation, when coupled with molecular beam mass spectrometry (MBMS), is exceptionally promising. This technique (1) allows the study of isolated particles of well-defined size; (2) solves the mounting problem for small particles with diameters ranging to below 10 μm ; (3) provides sufficient reacted or volatilized material to be analyzed by MBMS or, when applicable, spectroscopic techniques; and (4) permits good spatial and temporal resolutions. In addition to coal, this technique should be applicable to other materials for which time and/or spatially resolved data are needed for processes involving rapid heating of small particles.

In the laminar flame studies, equipment and techniques were refined so that concentration levels, depending on the species, of 1 to 10 ppm could be measured. It was demonstrated that flame stability and spatial resolution were adequate for detailed coal combustion studies, and that the devolatilization products and combustion intermediates were present in substantial concentrations in the reaction zone. This technique can therefore be used for a direct study of detailed combustion processes of various coals.

In addition to the experimental studies, a mathematical model was formulated that would incorporate the experimental data from the two classes of experiments. The physical parameters to be used to describe the coal combustion processes were selected, and the numerical methods partially developed. (Midwest Research Institute)

Synfuel Utilization

J.D. Hickerson, Coordinator

The objective of this project is the development of a technology base for the effective utilization of coal-derived liquid synfuels.

The problem of transient droplet vaporization in a hot convective environment was examined. The main objective was the development of an algorithm for the droplet vaporization that is simple enough to be feasibly incorporated into a complete spray combustion analysis and yet would also account for the important physics, such as liquid-phase internal circulation, unsteady droplet heating, and axisymmetric gas-phase convection. The model fuels studied were hexane, decane,

and hexadecane. A simplified liquid-phase model was obtained that is based on the assumption of the existence of a Hill's spherical vortex inside the droplet, together with some approximations made in the governing diffusion equation. A one-dimensional gas-phase model, which simplifies the analysis in the gas phase through representing the heat and mass transfer rates by an optimum average for the stagnation point region and the shoulder region of a droplet, was also developed. The results of coupling this simplified gas-phase model with the simplified liquid-phase solution were in good agreement with the results of a more detailed model. The present simplified model requires significantly less computing time than the more detailed model.

The use of the simplified model in a spray situation was also examined. Droplet heating and vaporization are essentially unsteady, and droplet temperature is nonuniform for a significant portion of its lifetime. The effects of different gas-phase and liquid-phase models on the vaporization behavior for a single isolated droplet, as well as for spray conditions, were studied. The feasibility of incorporating the present simplified model into a one-dimensional spray vaporization calculation was verified, demonstrating the potential usefulness of the model in an overall spray situation. The droplet vaporization characteristic can be quite sensitive to the particular liquid-phase and gas-phase models.

The simplified model has been extended to the multicomponent droplet case. The results of the present simplified model were compared with the results of the infinite diffusivity model and spherical diffusion limit model. Largely due to the neglect of the thermal and mass diffusion resistances, substantial differences in the vaporization behaviors between the infinite diffusivity model and the other two models were found.

The disagreements between the models at short times were caused by differences in mode of the thermal energy transfer; for the bulk of the droplet lifetime, the discrepancies were due to differences in the mass diffusion models. The disagreements between the present simplified vortex model and the spherical diffusion limit model were comparatively lessened by droplet vaporization.

Both the finite difference solution scheme and the ordinary differential equation formulation were used for the coupled-vaporization problem. The computational efficiencies of the two solution schemes were compared, and the ordinary differential equation formulation that eliminates

the spatial dependence from the problem was more efficient.

The results of the various models were compared with the existing experimental data. Due to large scattering in the experimental measurements, particularly the droplet diameter, no definite conclusion could be drawn based on the experimental data. Finally, certain research problems that are related to the present study have been suggested for future studies. (Carnegie-Mellon University)

A program was conducted to significantly expand the available data base at intermediate temperatures (about 1000K) on the oxidation characteristics of higher carbon number paraffins, including n-butane, isobutane, n-octane, and 2,2,4-trimethylpentane (isooctane). An earlier irreversible multistep semi-empirical model for n-paraffin oxidation, from similar work on propane, was also modified to account for major thermal dissociation effects (CO and H₂ as final products). By modifying only the fuel conversion rate to intermediate species, acceptable reproducibility of intermediate and final product evaluation at intermediate temperatures, and ignition delay phenomena at shock tube temperatures were achieved for n-butane, isobutane, and n-octane. Intermediate product characteristics for isooctane were different than those for the other fuels studied; the model considered was not extendible to this fuel.

The program continued expansion of understanding for the oxidation of simple aromatic structures through additional flow reactor studies on benzene, toluene, and ethylbenzene. As an important part of the aromatics effort, additional flow reactor oxidation studies were conducted on butadiene, one of the major intermediates formed in the oxidation of toluene and benzene. Ethylene, a species that is formed during the oxidation of aromatics and of many other hydrocarbons, was the focus of a detailed mechanistic examination that has led to the proposal of an in-depth oxidation model.

As part of a comprehensive analysis of the CO/H₂O/O₂ system, the kinetics of wet CO oxidation were studied in depth. Comparisons of model and experiment over a wide range of conditions showed that a detailed kinetic model always predicted qualitatively the trends of the experiments. The technique of Green's Function sensitivity analysis was applied to the detailed CO model, and the first-order sensitivity coefficients for all rate parameters were studied. (Princeton University)

IN-HOUSE RESEARCH AND DEVELOPMENT

ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT: DIRECT UTILIZATION

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 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 underway to evaluate various measurement techniques capable of monitoring the physical and chemical structure of deposits as a function of time.

Instrumentation required for the powder flow laboratory study is being set up and calibrated. The coals that will be used in the study have been identified. Samples will be obtained. Tests have been conducted in both the high-pressure coal flow test loop (HPCFTL) and the coal-water test loop facility (CWTL). Data taken in the HPCFTL will be used in a scale-up study. Tests in the CWTL were directed at confirming the impact of slurry pH on flow properties; this impact had been identified in previous laboratory work.

Combustion testing continued in the tunnel furnace. An air register with acceptable performance characteristics was designed and tested. Several sampling probes were tested; these probes are used to measure temperature and heat transfer characteristics within the furnace volume. Slag samples have been collected from various sources. X-ray diffraction analysis is underway on these samples. Mössbauer spectroscopy and magnetization measurements will be initiated next.

Dense-Phase Powder Characteristics

M.P. Mathur, Cost Account Manager

*J.I. Joubert, Chief,
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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 rate studies will be conducted.

Two machines, namely, a Soiltest Machine for measurement of shear properties of coal and a Permeability Tester for measuring permeability of the coal powders as a function of consolidation pressure, are being set up. Another machine that measures other powder flow characteristics, such as the compressibility, the aerated and bulk powder densities, the dispersibility, and the angles of repose, fall, and spatula, has already been set up for powder testing.

The coal types for these measurements have been identified. They are (1) Pittsburgh seam coal with at least three different ash contents, (2) Montana Rosebud coal, (3) anthracite, and (4) other eastern coals of interest. First, the powder characteristics of these coals will be determined as a function of particle size and coal moisture content. Then, various blends of two or more coals will be investigated. Concurrent with these tests, fluidizing characteristics of these coal powders and their blends will be determined to classify the powders in terms of Geldart's charts.

A literature survey of the field of dense-phase transport is being conducted.

A paper, "Dense-Phase Pneumatic Transport of Coal: Measurements and Analysis," was accepted for publication in a special issue of the Journal of Powder Technology on Coal.

Flow Characteristics of Coal-Based Fuels

D.J. Wildman, Cost Account Manager

J.I. Joubert, Chief,

Combustion Technology Branch

During the last quarter, tests were conducted in the high-pressure coal flow test loop (HPCFTL) and in the coal-water test loop facility (CWTL).

The HPCFTL was involved in a cooperative effort with the Southwest Research Institute (SWRI). The SWRI used the series of tests for instrumentation evaluation. The tests were conducted with Montana Rosebud coal. The moisture content of the coal was 4% for the first series and 8% for the second. After the cooperative effort with SWRI, more tests were conducted in the HPCFTL. High speed transient data were recorded during the changes in test conditions. The pressure loss data will be used in a scale-up study that involves data from the atmospheric pressure coal flow test loop facility (APCFTLF).

The Kay Ray densitometers were taken from storage and assembled for inspection by a service representative. Amplifier cards on both units were not functioning. The ion chamber of one of the detectors was missing. The heater control board and heater blanket had been removed from the other detector. The densitometers were to be used on the CWTL, but funds are not available to replace the missing parts.

The Rheology Laboratory has studied the effects of pH variation on viscosity of CWMs prepared with Pittsburgh seam coal. Wide variations in measured viscosity were found. A series of tests was designed for the CWTL in which the pH of the CWM was varied. The principle objective of this series of tests was to determine the effect of the pH on pressure loss across horizontal and vertical sections of pipe. Eastern Kentucky coal beneficiated to 2% ash, with a particle size distribution of 60% finer than 75 microns, was used in these tests. Initially, the pH of the mix was 4. The pH of the mix was increased with the addition of sodium hydroxide. Tests were conducted at mix pH's of approximately 4, 7, 8, and 10. The changes in the mix pH caused the horizontal pressure gradient to vary from 19 lb/ft²/ft to 29 lb/ft²/ft for flow rates of approximately 505 lb/min. Vertical pressure gradients varied from 37 lb/ft²/ft to 54 lb/ft²/ft. The large span in the pressure gradients for both test sections indicates the need of pH control to insure transportability of the mix. The reported vertical pressure gradients are computed by subtracting the static head from the

total pressure gradient. The difference in the magnitudes of the horizontal and vertical pressure gradients is due to the settling tendencies of the coarse particle size distribution.

A model was developed that predicts pressure gradient data taken from horizontal sections of pipe. The model divides the cross-sectional area of the pipe into two regions. Homogeneous flow is assumed in the top region, and nonhomogeneous flow is assumed in the bottom region. The details of the model will be presented at the Ninth International Technical Conference on Slurry Transportation. In the next quarter, the CWTL will be utilized in a study of secondary flow around bends. Work will be initiated on construction of a 1½-inch-diameter pipe loop for the APCFTLF.

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 (1) to investigate the effects that firing beneficiated and/or micronized coal in a pulverized or slurried form has on particulate processes occurring during combustion and (2) 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.

A computer program was developed to predict swirl number and axial velocities in an air register with primary and secondary air, the latter injected through a cascade of guide vanes. The program was used to extensively modify a burner for coal-water mixtures (CWM). This modified burner gave very stable combustion with commercial CWM. Combustion also appeared stable with CWM produced at PETC. The burner appears to produce high swirl, but it has not yet been determined how much gas recirculation there is in the center of the flame.

Previous burner air registers have had bearing problems. The new air register had stainless steel shafts turning in carbon steel bearings, which is not a desirable combination, although it appeared to work. To prevent future problems, one beryllium-copper bearing was substituted for carbon steel and tested satisfactorily. Other such bearings will be installed.

A group of three deposition probes was assembled and tested in the stack. They appeared to operate properly, but data are still being reduced.

Several sampling probes were developed and/or tested for use in the flame or stack. A sonic aspirated thermocouple was developed for the flame. Tests showed it agreed approximately with a subsonic commercial aspirated thermocouple but was more convenient to use and less susceptible to plugging with ash. An air-cooled isokinetic probe was developed to overcome problems with water-cooled probes and was tested in the stack. A cascade impactor was used successfully to sample the stack. After careful adjustment, a water-cooled solid-sampling probe was used successfully in the flame.

Next quarter, a more reliable slurry feed system will be installed, as well as eleven more beryllium-copper bearings in the air register. Material balances will be rechecked. Combustion tests of CWM produced from one coal seam will be initiated, varying the particle size and the amount of physical coal cleaning.

**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.

The importance of iron oxides to deposit formation and growth is indicated by several researchers. Experimental evidence clearly indicates

that several distinct layers develop in a deposit over time, exhibiting differing chemical compositions and physical characteristics. It is also known that various forms of iron, iron oxides, and iron sulfates exhibit various types of magnetic spin ordering behavior, such as ferromagnetic, paramagnetic, or antiferromagnetic. The magnetic Curie temperature in the iron-oxygen and iron-sulfur systems is a function of the composition and of the environment (oxidizing or reducing) in which the slag is deposited. A literature survey of magnetic oxide properties of various constituents in coal slag is in progress.

Four slag samples obtained from various combustion units were collected for magnetic property measurements. X-ray diffraction analysis, a very powerful and versatile tool to characterize the minerals in coal, is underway on these samples. It is known that the X-ray diffraction pattern of a mineral is similar to fingerprints, and positive identification of various iron oxides can be obtained from the patterns. Moreover, one can also ascertain the proportions of constituent phases in a bulk sample in a quantitative fashion. Mössbauer spectroscopy and magnetization measurements as a function of temperature (300°C to 600°C) will be started next.

A visit to Westinghouse Electric Corporation was made in November 1983 to learn about various eddy current techniques available for detecting magnetic oxides in the slag matrix. The above-mentioned slag samples will be analyzed using this technique.

In order to prepare synthetic slags, various oxides found in coal slag were ordered from some local vendors. An AC vertical-tube furnace that is capable of reaching a temperature of 1050°C was acquired. The furnace is in the process of being set up.

**ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT:
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 thermo-physical properties of high boiling and nondistillate coal-derived materials.

The nature of the heavy recycle solvents and products from two-stage liquefaction experi-

ments at the LUMMUS and Wilsonville PDU's was further investigated. Differences have been found in the saturate and base fractions of ITSL solvents from the two operations, which may in part be related to different second-stage hydrotreater conditions. Average structural parameters were determined for benzene-insoluble fractions of ITSL and NITSL (non-integrated two-stage liquefaction) first-stage products derived from Illinois No. 6 coal at different reaction severities.

Measurement protocols for implementing fundamental investigations of coal-solvent interactions by ^{13}C pulsed NMR techniques have been established. Base-line studies were completed on several bituminous coals to be used in further experimentation.

The effect of the promoter on the Raman active $\text{Mo}=\text{O}$ stretching modes in $\text{NiO-MoO}_3/\text{Al}_2\text{O}_3$ catalysts was studied. The frequency of the $\text{Mo}=\text{O}$ stretching band was independent of Ni concentration immediately after O_2 calcination but decreased upon exposure of the catalyst surfaces to H_2O . The band intensity was dependent on the Ni concentration.

In research related to the development of thermophysical property correlations, general inspection properties of an H-Coal product distilled into 50°F cuts (pseudo-components) from 400°F to 850°F were determined. Further chromatographic separations and spectrometric measurements are in progress. All pertinent process streams at the Wilsonville Advanced Coal Liquefaction Facility were sampled to provide a well-documented set of samples for study. The molecular size distribution and functionality of vacuum bottoms fractions from the PETC Fractional Distraction Unit have been investigated by liquid chromatography. Initial tests of a gas chromatographic procedure for determining the activity and distribution coefficients for a distillate component in the presence of a vacuum bottoms fraction were completed.

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 utilized 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.

A better quantitative estimate of the total potentially donable hydrogen in ITSL solvents can be made by nuclear magnetic resonance (NMR) procedures if the contributions of saturates to the total sample spectra are removed. Heavy ($650^\circ\text{F}+$) recycle vehicles derived from Illinois No. 6 (Burning Star) coal during ITSL operations at the LUMMUS PDU and Wilsonville Advanced Coal Liquefaction Facility were split into saturate and nonsaturate fractions by column chromatography. Both solvents contain relatively high concentrations of saturates that contribute significantly to the total hydrogen content but little donable hydrogen under first-stage liquefaction conditions. The saturates in both vehicles are primarily cyclic or highly branched. The LUMMUS solvent appears to be depleted in straight-chain saturates of carbon number less than C_{25} relative to the Wilsonville solvent.

The nature of the basic nitrogen components in the LUMMUS and Wilsonville ITSL solvents was further investigated after isolation by cation exchange column chromatography and derivatization with trifluoroacetyl chloride. Structural differences between the high molecular weight bases in the two solvents were determined by high resolution mass spectrometry (HRMS) utilizing direct probe introduction at 350°C . The most striking feature of the LUMMUS bases was the high concentration of parent structures in a given homologous series, while the Wilsonville bases display extensive hydrogenation in all homologous compound series. About 25% of the observed compounds containing a single nitrogen in the LUMMUS solvent derivatized, indicating the presence of an active hydrogen (amine) functionality. More than 40% of the observed nitrogen bases in the Wilsonville solvent derivatized. These results are consistent with the net hydrogen content of the solvents and respective second-stage hydrotreater conditions during production of the solvents.

A comparison of structural features of Burning Star coal and first-stage products derived therefrom under different reaction severities is in progress. Coal samples from both LUMMUS and Wilsonville gave identical carbon aromaticity values, 0.71, by ^{13}C -CP/MAS NMR measurements. To minimize contributions from ITSL solvents, which are largely toluene-soluble, investigation of the first-stage products has concentrated on

toluene-insoluble fractions. The hydrogen contents of several Wilsonville NITSL and ITSL product fractions fell between 5.0% and 5.6% (maf) regardless of reaction severity or mode of operation. Number average molecular weights (VPO, pyridine, 80°C) from 1100 to 1200 amu were obtained for toluene insols in LSRC and 1500 to 1600 amu for SRC and ITSL hydrotreater feed fractions. Carbon aromaticities were ~ 0.8 but increased with reaction severity in NITSL fractions. According to calculated average structural parameters, the toluene-insoluble fractions consist of high molecular weight, multiring cluster components with short alkyl substituents. The estimated average aromatic + heterocyclic ring cluster size is ~ 5 rings.

Derivatization procedures are also being used to facilitate study of the heteroatom functionalities in first-stage products. Trifluoroacetyl derivatives of nitrogen base and phenolic acid fractions of heteroatom-rich LSRC's from low and moderate severity Wilsonville NITSL runs were prepared. Components ranging from 2 through 7 rings were observed by HRMS in both derivatized bases (amines) and nonderivatized bases. About 30% of the bases observed also contained an oxygen functionality.

Next quarter, calculations of the total donable hydrogen in the LUMMUS and Wilsonville ITSL solvents will be completed, utilizing a combination of ^1H and ^{13}C NMR and elemental analysis data on the saturate fractions and total solvents. Conventional ^{13}C -CP/MAS and dipolar dephasing NMR techniques will be applied to Illinois No. 6 coal and product fractions to not only determine carbon aromaticities but also estimate the relative proportions of protonated and nonprotonated and methyl carbons. Investigation of the heteroatom functionality by acylation procedures will be continued. An investigation of "primary" preasphaltenes from liquefaction of Kentucky 9,14 coal under mild conditions will be initiated at PETC.

Structural Mobility of Treated Coals and Coal Slurries

R.F. Sprecher, Cost Account Manager

*H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective of the project 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 utilizing magnetic resonance techniques to study changes in the relative freedom of motion of coals after careful pretreatment over a range of temperature 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 Brüker CXP100 NMR spectrometer.

Base-line studies on the Illinois No. 6 coal used in the Lummus SCT process, the Illinois No. 6 coal used in the Wilsonville two-stage process, River King (Illinois No. 6) coal, and Blacksville No. 2 (W. Va. Pittsburgh seam) coal have confirmed the observations of Snape et al. that f_a values determined by cross-polarization magic angle spinning CP-MAS NMR do not always agree with rank as determined by carbon content. Systematic differences in f_a by CP-MAS and f_a by classic Block decay measurements were found in the course of the base-line study. The origins of those differences is being sought.

During the next quarter, several samples of Illinois No. 6 coal and the Pittsburgh seam coal used for the base-line study will be allowed to imbibe the vapors from pyridine, tetrahydroquinoline, and tetrahydrofuran. Measurements by NMR, including dipolar dephasing measurements, will be made at intervals during the swelling process for each coal-solvent pair. The influence of the various polar solvents on the coal matrix will be determined.

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 thermo-physical properties of synfuels, is twofold. The first is to identify, develop, and apply advanced

methods of structural characterization of synfuels that will provide data that will 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 (PCT) 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 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. General inspection properties, including CHONS, VPO molecular weight, FPD molecular weight, water content, pycnometric specific gravity, viscosity, and simulated distillation by gas chromatography have been obtained for most of these pseudocomponents. Various advanced chromatographic and spectrometric analytical measurements are either currently underway or planned for each fraction. The carbon and proton distributions are being measured by ¹³C and ¹H NMR. Infrared spectroscopy is being used to survey the functional groups present, to quantitatively determine the OH concentration, and to estimate the amounts of N-H in each pseudocomponent. Mass spectrometry is being used to analyze the samples, employing low ionizing voltage and high resolution to obtain precise mass, and thus molecular formulae, on individual constituents present in each pseudocomponent. Low resolution field ionization mass spectral measurements are being made on select pseudocomponents to obtain mass information on the less volatile fractions.

During the past quarter, work was continued on evaluating two chemical class fractionation schemes for their ease of use, reproducibility, difficulty of performance, and overall ability to

separate synfuels into chemical classes. The schemes being evaluated were originally reported by scientists at Brigham Young University and the National Institute for Petroleum and Energy Research. The evaluations should be complete next quarter, and an appropriate scheme will be selected and applied to the separation of the various H-Coal pseudocomponents. It is quite conceivable that the separation scheme finally utilized may be a derived one that incorporates the strengths of both schemes currently under evaluation. Nevertheless, each distillate fraction may present its own unique set of problems and require additional modifications to the scheme for optimization.

Personnel from PETC sampled all pertinent sample streams at the Wilsonville, Ala., pilot plant during the second week of December 1983. Nearly 1/2 ton of well-documented materials is currently in transit to PETC. These materials will be distilled at PETC; a Podbielniak distillation apparatus will be used to generate suitable pseudocomponents. The Podbielniak apparatus is currently undergoing substantial modification to perform the required distillation.

During the quarter, there also has been substantial progress in other areas within the project. For example, a multidimensional gas chromatograph has been purchased, installed, and tested. Preliminary indications are that the instrument will provide analytical information that is not easily available by other means. A manuscript describing various spectral approaches to the detailed characterization of vacuum still bottoms is in internal review. The 850°F vacuum still bottoms from H-Coal has been separated into various classes of organic compounds using the previously described separation schemes. Each fraction is undergoing further analyses. The postdoctoral member of the project team assisted the PETC Project Management Representative in a review of the BETC PCT properties program. Lastly, liaison with the Coal Conversion Engineering Branch is being continued, with emphasis on (1) the status of the supercritical distillation unit and (2) discussions of project relevance to engineering needs.

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-

distillate 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, characterization of vacuum bottoms fractions produced in a companion project (Liquefaction Bottoms Fractionation) has begun. Three samples spanning the suite of fractions obtained from the Fractional Distraction Unit were used to develop procedures for investigating molecular size distribution and functionality. These particular fractions were previously characterized by field ionization mass spectrometry (FIMS), vapor pressure osmometry (VPO), proton NMR, infrared spectroscopy, and elemental analysis, thus providing reference data for the liquid chromatographic separations. Molecular size distributions were obtained using a mixed-bed PL-gel column. The trends observed parallel those obtained by FIMS. The VPO data have not been completely consistent with the latter two methods. The deviations are likely due to the fact that VPO measurements are sensitive to low levels of volatile components. This technique is also highly operator dependent. The initial investigation of the functionality of the fractions was performed on a Bondapak-NH₂ column. The most noticeable variation is in the neutral aromatic species. As the fractions become "heavier" (higher molecular weight), the relative amounts of neutral aromatic components are observed to decrease. A fluorescence emission scan of the neutral aromatic component in a heavier fraction indicates that phenanthrene- or pyrene-type systems remain, whereas the population of two- and three-ring linearly condensed systems is much lower. These cursory results are being used to direct a more detailed investigation of vacuum bottom fractions.

During this quarter, the gas chromatographic experimentation directed at determining selected

thermodynamic properties of binary distillate/bottoms mixtures was started. The procedure involves using headspace sampling to measure activity coefficients and distribution coefficients for a distillate component in the presence of a vacuum bottoms fraction produced in the FDU. Most of the effort was directed at verifying the accuracy of the equipment to be used with respect to published values. A mixture of ethanol/heptane was used for this evaluation. The first results were not acceptable. After discussion with the vendor, a different method of controlling the pressurization of the headspace sampler was incorporated. Repeat analysis of the model system resulted improved agreement with published data. Further optimization of this technique is being conducted before introducing mixtures containing vacuum bottoms.

Plans for the next quarter include continuation of both areas of chromatographic investigation. In the liquid chromatographic research, the emphasis will be on continuing the development of the molecular size separations using higher resolution columns and on utilizing fluorescence scanning and ultraviolet wavelength ratioing methods to probe the composition of the resulting components. The measurement of activity coefficients of distillate components in mixtures with vacuum bottoms fractions using headspace sampling will be attempted after some additional work with pure compounds.

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.

The Raman frequency shifts for Mo=O stretching modes as the Ni promotor concentration is increased in NiO-MoO₃/Al₂O₃ have been reevaluated. This reevaluation was done with the catalysts exposed to controlled environments of O₂ and H₂O. After O₂ calcination, the Mo=O

stretching frequency remains at 1007 cm^{-1} , independent of the Ni concentration. Exposure of the calcined catalysts to H_2O decreases the $\text{Mo}=\text{O}$ stretching frequency to a position similar to that observed in the air-exposed catalysts. Although the position of the band due to $\text{Mo}=\text{O}$ stretching is independent of the Ni concentration, the intensity of this band is dependent on the Ni concentration.

The origin of the $\text{Mo}=\text{O}$ band displacement is under further investigation to determine whether it is the result of hydrogen bonding, coordination sphere expansion, or other possible interactions. During the next quarter, a 15% $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst will be exposed to controlled environments of polar and nonpolar compounds having strong and weak hydrogen-bonding characteristics.

ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT: MECHANISTIC ASPECTS OF LIQUEFACTION

B.C. Bockrath, Coordinator

Exploratory experiments were begun in small autoclaves using water as a prime component of coal liquefaction feed slurries. High conversions were obtained using a reactive Illinois No. 6 coal with minor amounts of water and a conventional recycle solvent added to make the feed. The ratio of coal/water was 70/30, similar to that used in making pumpable coal-water mixtures for combustion. The results encourage efforts to find ways of reducing the need for recycle solvents.

In related experiments using low rank coal, the effects of steam pressure, organic solvents, and reducing gas were determined. Conversion of lignite increased with increasing steam pressure. Replacing part of the water with organic solvents such as 1-methylnaphthalene gave the twin benefits of reduced operating pressure and increased conversion. Carbon monoxide produced a markedly higher conversion than hydrogen when used as the reducing gas.

In order to investigate the initial reactions in conventional coal liquefaction, conditions were determined for producing large yields of primary preasphaltenes using slow heat-up times to 350°C . Similar conversion values were obtained using three synthetic vehicles of different hydrogen donor ability. In contrast, earlier work showed that donor quality has a significant effect on conversion in rapid heat-up, short residence time liquefaction. Thus, hydrogen might be conserved by using slower heat-up rates with less highly hydrogenated solvents.

In cooperation with researchers at the Pennsylvania State University, a series of coal samples subjected to hydrogenation with no added solvent has been analyzed by ^{13}C NMR spectroscopy using PETC's recently acquired spectrometer for solids. There is a net increase in aromaticity in cases both with and without added ammonium

molybdate catalyst, suggesting that aromatization reactions predominate over hydrogenation reactions at 400°C if solvent is not present.

Investigations 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.

This quarter, the recently acquired nuclear magnetic resonance (NMR) spectrometer for obtaining ^{13}C spectra of solids was used to determine the aromaticities of residues (methylene chlorine insolubles) generated in an investigation of the dependence of hydrogen utilization on coal reactivity. Some initial effort was spent optimizing performance of the new instrument and comparing aromaticities obtained by different ^{13}C NMR procedures. This work was necessary to obtain some measure of the reproducibility of the aromaticity values.

The residue aromaticities are now being used to assemble a comparison of the utilization of hydrogen in a more reactive coal (Illinois No. 6) and less reactive coal (Blacksville) over a range of temperatures from 325°C to 425°C . Preliminary results indicate that there are differences between the two coals, but comparison with earlier

work also indicates that there may be a larger change associated with a switch in solvents from a centrifuged liquid product to a lighter SRC-II heavy distillate. Since the required experimental data on this set of experiments have now been acquired, calculations and interpretation should be completed next quarter.

In cooperation with researchers at the Pennsylvania State University, a series of coal samples (Ohio No. 5) subjected to dry (no added solvent) hydrogenation at 400°C with and without added ammonium molybdate has been analyzed by ¹³C NMR. The results clearly indicate that under these conditions there is a net increase in aromaticity upon hydrogenation in both the catalyzed and the uncatalyzed cases. This suggests that aromatization predominates, even in the presence of catalyst, at 400°C if solvent is not present.

Next quarter, an autoclave study of the effect of catalysts on the utilization of hydrogen in the presence of liquefaction solvent will be started. These experiments will compare the utilization profiles in the presence of a good liquefaction catalyst having low hydrogenation activity (SnCl₂) and a good liquefaction catalyst having high hydrogenation activity (Co or Mo).

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 determine the course of hydrogen transfer reactions that involve the hydrogen atom, and to determine the relationship between coal conversion and the rheological properties of coal/solvent slurries at elevated temperatures.

Investigations of the role of hydrogen in coal liquefaction can be facilitated greatly by the use of deuterium and deuterium-labeled compounds. Analysis of the products from these experiments requires differentiation between molecules that differ only in substitution of deuterium for hydrogen atoms. Recent experiments have shown that rapid and simple separations are possible in some cases using capillary gas chromatography.

A mixture of toluene, toluene- α -d₃, and toluene-d₈ was separated on a 50- x 0.2-mm-i.d. methyl-

silicone-coated glass capillary column. Base-line resolution was achieved between toluene-d₈ and toluene- α -d₃ or toluene, but resolution of the latter two compounds was not quite complete.

The ease of separation of deuterium-substituted compounds is quite sensitive to their molecular structure. For example, fluorene-9,9-d₂ was separated from fluorene, but anthracene-9,10-d₂ could not be separated from anthracene. The relationship between molecular structure and the degree of separation is not yet well enough understood to allow for a satisfactory explanation of these differences. However, some facts are known. Inverse isotope effects have always been observed, i.e., deuterated compounds elute before non-deuterated compounds. The separation factor for toluene and toluene-d₈ increased as the column temperature was reduced. From the temperature dependency, the difference between these two compounds in the heat of absorption on the methylsilicone coating of the column was calculated as only 16 cal/mole. This small difference points out the fact that the separation is based on subtle effects.

Exploratory experiments were begun with coal liquefaction in small autoclaves in which water was used as a prime component of the feed composition. Such systems might lead to novel process concepts that employ water rather than conventional recycle solvents as a vehicle for transport of coal into reactors and as a medium for liquefaction reactions. Initial results using a reactive Illinois No. 6 coal indicate that high conversions can be obtained using feed slurries composed of mostly coal with minor amounts of added water and conventional recycle solvent. A conversion of 92% (based on residue left after tetrahydrofuran extraction) was achieved by heating a mixture of coal, water, and solvent to 427°C for one hour under 2700 psi hydrogen partial pressure with 0.02 wt% ammonium molybdate added as catalyst. Total operating pressure was estimated to be 4500 psi. Water and recycle solvent obtained from operations of the Lummus two-stage liquefaction process were added as 30% and 25% of the coal weight, respectively. Increasing the amount of organic solvent had little effect on conversion, but removing it entirely reduced the conversion to 80%. These results indicate that practical levels of coal conversion can be obtained using very low amounts of organic recycle solvent and in the presence of water used in the amount now commonly employed to make coal/water mixtures that are pumped as liquid fuels for combustion furnaces.

In the next quarter, hydrogen utilization under low severity liquefaction conditions will be investigated by generating liquefaction products for detailed analysis by NMR spectroscopy. The influence of assorted catalysts on hydrogen redistribution will be determined by comparison of results obtained after using several different catalysts. The investigation of hydrogen atom transfer reactions will be conducted using deuterium-labeled compounds to identify possible sources of hydrogen atoms under liquefaction conditions.

**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 (referred to as initially formed or primary preasphaltenes) using previously developed techniques, and by isolating and characterizing subsequent hydroliquefaction reaction products involving initially formed preasphaltene 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.

Conditions for preparing "primary preasphaltenes" under low-severity conditions have been determined. Preparation of primary preasphaltenes under low-severity conditions will involve a slow heat-up (1°C/min) with a reaction time of 1 hour at 350°C. Under these conditions, approximately 75% of the coal is converted to THF-soluble material, of which 55% to 60% of the coal is preasphaltene material.

Preparation of primary preasphaltenes from Western Kentucky 9/14 coal under low-severity conditions, using three different synthetic vehicles of differing donor ability, gave similar conversion values. The compositions of the three synthetic vehicles were as follows:

Vehicle I
33% 1-Methylnaphthalene
20% Phenanthrene
10% Pyrene
13% m-Cresol
4% Quinoline
20% Tetralin

Vehicle II
50% Phenanthrene
40% Pyrene
10% 9,10-Dihydrophenanthrene

Vehicle III
40% 1-Methylnaphthalene
30% Phenanthrene
10% Pyrene
20% Tetralin

This is very different behavior from that observed in rapid heat-up, short residence time liquefaction, where donor quality has a significant effect on conversion. Thus, it may be possible to compensate for poor donor quality by going to slower heat-up rates and thus conserve hydrogen.

In studying the effect of time on conversion and preasphaltene formation under these low-severity conditions, i.e., slow heat-up and 350°C maximum temperature, it was found that conversion reached the maximum value for that temperature in one hour or less, with no appreciable increase at longer time or, as noted, with improvement in donor quality. This is further evidence that most of the bond breaking necessary for primary coal liquefaction requires less energy than is commonly assumed. Incremental increases in reaction temperature (82% conversion at 375°C) achieve increasingly smaller additional conversion. These results are consistent with a coal structure containing a variety of bonds with a spectrum of cleavage activation energies rather than the singular energy relationship usually invoked.

The stability of the primary preasphaltene is being examined. Several reports from other research efforts have indicated that preasphaltenes "age," or at least exhibit loss of solubility with time. Initial indications are that these primary preasphaltenes may be extremely sensitive to this aging phenomenon. This behavior will be examined as one of the characteristic properties of these initial liquefaction products. It also implies that primary preasphaltenes must be characterized rapidly following preparation.

**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 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 carbon monoxide/water systems.

A series of base-line experiments was conducted to determine the conversion and extent of extraction of three coals, using water at supercritical conditions. The data, summarized in Table 9, show that removal of soluble materials, plus

water and gas, was 49% for Beulah Lignite and 38% for Wyodak subbituminous coal, but only 2% for Western Kentucky 9/14 bituminous coal. All of these coals were treated for 15 minutes at 380°C and pressures near 3200 psi in a minireactor. The pressure developed using Western Kentucky 9/14 was slightly less (3100 psi) because of less gases evolved by this coal during the thermal steam treatment. Part of the observed conversion is due to simple extraction, but at 380°C, a considerable

Table 9.
Coal Liquefaction in the Presence of Water at 380°C

Coal	g	Solvent	g	Gas, psi	Operating Pressure	Time, min	Conv. %	THF Sol	CH Sol	pa ^a
Lignite ^b	1.5	H ₂ O	9.6	None	3200	15	49			
Wyoming	1	H ₂ O	10	None	3200	15	38			
W. Ky. 9/14	1	H ₂ O	10	None	3100	15	2			
Lignite	1.5	H ₂ O	8	None	2400	15	38			
Lignite	1.5	H ₂ O	7	None	1500	15	22			
Lignite	1.5	H ₂ O	4	None	800	15	31			
		MeN ^c	3							
Lignite	1.5	H ₂ O	4	None	1700	15	45			
		Tet ^d	3							
Lignite	1.5	H ₂ O	3.5	None	2500	5	9	64	36	18
		Pip ^e	3.5							
Lignite	1.5	H ₂ O	3.5	None	1500	5	61	89	E-O	67
		THQ ^f	3.5							
Lignite	3	H ₂ O	7	None	2300	5	NA	15	10	9
Lignite	3	H ₂ O	3	CO, 800	3300	5	28	21	19	1.4
Lignite	3	H ₂ O	3	CO, 800	3100	5	42	44	26	16
		THQ	0.3							
Lignite	3	H ₂ O	3	H ₂ , 800	3300	5	23	23	13	3.5
		THQ	0.3							

^aPreasphaltenes plus asphaltenes

^bBeulah Lignite containing 26.0% water (other coals dry)

^c1-Methylnaphthalene

^dTetralin

^ePiperidine

^fTetrahydroquinoline

part of the conversion is believed to be a result of hydrolysis and cleavage of some of the weaker bonds in the coal.

The effect of steam pressure on conversion at 380°C was also determined for lignite. At pressures of 2400 psi and 1500 psi, the conversion decreased to 38% and 22%, respectively. This decrease is the expected response to the decreased solvent effectiveness of the lower density steam at supercritical temperatures. At the three pressures indicated in Table 9 for these first three experiments, the water vapor densities are ≈ 0.3 , 0.23, and 0.15, respectively. The measured vapor pressures appear lower than expected; this is probably a result of condensation of some of the water in the cooler parts of the apparatus.

Replacement of part of the water with organic solvents below their critical temperature had the beneficial effect of reducing the operating pressure while increasing the extent of conversion. Using 1-methylnaphthalene, the operating pressure was only 800 psi, and the conversion was 31%. With tetralin, a 45% conversion was obtained at a pressure of 1700 psi.

The next two tests used the effective coal solvents piperidine and tetrahydroquinoline in conjunction with equal weights of water. Extensive reaction of these solvents with the coal oc-

curred. Considerable adduction of the nitrogen bases was indicated by the discrepancy between conversion values and the considerable amounts of tetrahydrofuran-soluble, tetrahydrofuran-soluble—cyclohexane-insoluble (preasphaltene-asphaltene fraction), and the cyclohexane-soluble oil recovered and isolated in these two experiments.

The last three experiments determined the effect of reducing gases on the conversion and product distribution. In order to keep the pressure near 3,000 psi, the amount of water added was reduced to 3 grams. (The water in the lignite contributed another 0.78 grams.) In the absence of an added catalyst and an initial CO pressure of 800 psi, the conversion of lignite was 28%. The addition of 0.3 gram of tetrahydroquinoline as a catalyst increased the conversion to 42%, and the yield of the preasphaltene-asphaltene fraction increased considerably. Replacing the CO by H₂ resulted in conversion of only 23%, illustrating the greater effectiveness of CO for low rank coals.

In summary, replacement of part of the water by organic solvents or CO resulted in improved extraction-conversion of lignite. A more detailed analysis of the liquefaction products, in progress, may provide clues to changes in liquefaction mechanisms in going from aqueous to aqueous-solvent-reducing gas systems.

ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT: ENVIRONMENTAL ASPECTS OF FOSSIL FUEL COMBUSTION

B. 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 Precipitation.

During the past quarter, considerable time was spent in coordinating the work of the several projects associated with the Deep Creek Lake Acid Rain Field Experiment. These are discussed in some detail.

In the final report of his feasibility study on "Boron as a Tracer of Aerosol from Combustion of Coal," K. Rahn, of the University of Rhode Island, showed that the ratio of gaseous atmospheric boron to sulfur dioxide, B/SO₂, correlates well with the influence of coal combustion on the sample and that "coal is by far the major source of both gaseous boron and SO₂ in coal-burning

areas." Also, Rahn has recently reported data that indicate that local sources in the Northeast contribute significantly to Northeastern aerosol.

Three tests were conducted to examine sulfate emissions from the combustion of fuel oil. The samples have been analyzed by ion chromatography, and emission factors will be calculated during the next quarter.

Acid Precipitation Studies
Y.S. Pan, Cost Account Manager
B.D. Blaustein, Chief,
Process Sciences Branch

During this reporting period, analyses of aerosol and rain samples collected during the Deep Creek Lake Acid Rain Field Experiment have been initiated, and sampling of plume par-

ticulates has continued. The U.S. Environmental Protection Agency (EPA), Electric Power Research Institute (EPRI), and the Ford Motor Company participated in and coordinated the Deep Creek Lake Experiment. The objectives of the experiment were to test the assumptions for the source apportionment of aerosol particles transported from sources to receptors and to determine the relationship, if any, between acid deposition and aerosol pollutants. During the experiment, size-segregated aerosol samples at the receptor site were collected by the Environmental Center of the Martin Marietta Corporation using a micro-orifice impactor (MOI). Selected samples are being analyzed by X-ray fluorescence (XRF) at EPA's Environmental Sciences Research Laboratory. Size-segregated aerosol samples in the plumes of emitting sources have been collected by the Virginia Polytechnic Institute and State University (VPI & SU). Plume samplings of a coal-fired power plant at Pleasants, W. Va., and of a paper mill at Chillicothe, Ohio, were also obtained.

The University of Minnesota, who constructed and calibrated the two MOI's used for the Deep Creek experiment, submitted a quarterly report providing detailed design data of the MOI's. Presently, they are investigating the problems experienced by VPI & SU and preparing the calibration curves. Since the MOI is newly developed equipment for collecting size-segregated aerosols, additional investigation will be required to assess various characteristics of this kind of equipment. The University of Michigan, who provided meteorological support during the field experiment, has computed back trajectories for each day in August using the upper-air data (850 mb level), roughly 1500 meters above mean sea level, from nine selected National Weather Service radiosonde stations. Additional calculations for surface trajectories are underway.

For receptor-model studies such as the Deep Creek Lake Experiment, one needs source signature data for as many elements as possible, especially trace elements, in order to identify sources of the pollutant aerosols. Because XRF is not very sensitive for some of the trace elements that are most useful for identifying particles from coal-fired power plants, a study proposal has been evaluated at PETC for using instrumental neutron activation analysis (INAA); INAA is highly sensitive for a number of elements that will provide the best signatures for identifying particles. Detailed chemical elemental analyses of acid precipitation samples have been hindered by low concentration levels, suspended solid particles,

etc., in the samples. Analytical techniques are being developed and/or optimized for analyzing such samples. Currently, the Analytical Chemistry Branch at PETC is developing procedures for analyzing for Pb, Cd, and As by atomic absorption (AA). A sampling station is being established at a PETC site to collect acid precipitation samples for use in developing new sampling and analytical procedures and experimental methods for establishing source-receptor relationships.

In the final report of his feasibility study on "Boron as a Tracer of Aerosol from Combustion of Coal," K. Rahn, of the University of Rhode Island, showed that the ratio of gaseous atmospheric boron to sulfur dioxide, B/SO₂, correlates well with the influence of coal combustion on the sample (see Table 10) and that "coal is by far the major source of both gaseous boron and SO₂ in coal-burning areas."

In another study using data for seven elements, Se, As, Zn, Sb, In, and non-crustal V and Mn, as tracers of distant regional pollutant aerosols, Rahn has found evidence that midwestern aerosol is strongly enriched in S and Se. First estimates of regional contributions to Northeastern aerosol of summer, based on the six element ratios as interpreted by Rahn, reveal that Northeast is responsible for at least 80% of the pollution-derived Zn, Sb, Mn, and V (rest from Midwest); 30% to 50% of the As and In (rest from smelters and Midwest); and roughly half (40% to 65%) of the Se and sulfate (rest from Midwest). Thus, local sources in the Northeast contribute significantly to Northeastern aerosol.

Personnel from this project attended the Conference on Acid Rain at Chicago, Ill., November 8-9, and Air Pollution Control Association's course on "The Use of Long-Range Atmospheric Transport Models in Reducing Acid Deposition" and its Specialty Conference on 'The Meteorology of Acid Deposition' at Hartford, Conn., October 16-19, 1983. Bernard D. Blaustein gave a lecture on Acid Precipitation at the University of Pittsburgh Department of Chemical Engineering on November 22.

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

Table 10.
B/SO₂ Ratios from Progressively Weakening Influence of Coal Combustion

Site	Nature of Sample	Range of B/SO₂(x10⁻³)
West Virginia	Stacks of two coal-fired power plants	0.3 — 1.1
Eastern Ohio	Freshest ambient measurements	0.5 — 1.4
Allegheny Mountain, Pennsylvania	Stronger coal episode	0.7 — 1.6
Allegheny Mountain, Pennsylvania	Weaker coal episode	1.4 — 2.7
Allegheny Mountain, Pennsylvania	Air from north and east	10 — 20

emissions from industrial coal combustion. These emission factors will be developed from test data taken during combustion tests at PETC.

During the past quarter, three tests were conducted to examine sulfate emissions from the combustion of fuel oil. A shakedown test of the controlled condensation sampling train (CCS) was conducted on the 20-hp boiler. A second combustion test was performed using the 20-hp boiler fired with No. 2 fuel oil. During this test, triplicate samples were obtained. Near the end of the quar-

ter, a single sample was obtained from a combustion test on the 700-hp boiler fired with a 0.3% sulfur No. 6 fuel oil.

The samples from the sampling train have been analyzed using ion chromatography. Emission factors will be calculated during the next quarter. Additional tests in both the 20-hp and 700-hp boiler are planned for the next quarter. The CCS train will again be used to collect sulfates. In addition, the sampling activity for chlorides and fluorides will be initiated on the 500 lb/hr unit.

COAL PREPARATION

A.W. Deurbrouck, Coordinator

Gravimetric testing of a sample of Waynesburg bed coal from Monongalia County, W. Va., showed that crushing from 1 1/2-inches down to 325-mesh top size and separating at 1.60 specific gravity would provide a significant pyritic sulfur reduction of 89% (from 1.33% down to 0.15%).

Pyrite size distribution, maceral analysis content, and degree of association of pyrite particles with coal have been determined on 11 samples of Pittsburgh bed coal crushed to 14-mesh top size.

During this quarter, work continued on the preparation of several sulfur-containing (thiophenic) polymers for use in studying various chemical desulfurization processes. These polymers will be calibration standards for the controlled-atmosphere programmed-temperature apparatus

that is being used to analyze for organic sulfur in coal by a direct method.

All of the references for a bibliography on selective coalescence have been gathered and cross-checked. Also, during this quarter, work was begun on the development of laboratory test procedures for conducting selective coalescence tests.

In a continuing program of flotation tests with low-rank coals, fatty acids, such as oleic acid, isostearic acid, and tall oil, are being used (along with fuel oil and MIBC when needed) in an effort to improve ash reduction and pyrite rejection.

A simple closed-system apparatus for preparing a coal-based binder in a controlled, reproduci-

ble way was constructed. Using a new binder formulation, coal pellets with acceptable strength and stability characteristics were produced. A satisfactory yield of 70% to 80% usable bituminous coal pellets was obtained by means of water addition to the pelletization mixture.

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.

Gravimetric testing was completed on a raw coal channel sample of Waynesburg bed coal collected in Monogalia County, W.Va. The sample was crushed to 1½-inches, ¾-inch, and 14-, 65-, 200-, and 325-mesh top sizes, and float-sink tested at 1.30, 1.40, and 1.60 specific gravities of separation (Table 11). Figure 1 plots the pyrite sulfur content of the float 1.30 and 1.60 specific gravity products for the coal samples crushed down to 325-mesh top size. The data show that crushing from 1½-inches to 325-mesh top size and separating at 1.60 specific gravity would provide a significant additional pyritic sulfur reduction of 89% (from 1.33% to 0.15%). The corresponding additional SO₂ reduction would be 45% (from 3.8 lb of SO₂/MM Btu to 2.1 lb of SO₂/MM Btu). Similar crushing and separating at 1.30 specific gravity show that an optimal pyritic sulfur content of 0.10 would be obtained at 65-mesh top size, and additional crushing would be of minimal benefit.

Pyrite Size Distribution

*J.T. Wizzard, Cost Account Manager
A.W. Deurbrouck, Chief,
Coal Preparation Branch*

The objectives of this study are to (1) determine the pyrite size distribution in a number of commercially important utility coals and attempt to correlate pyrite particle size with percent pyritic sulfur reduction, and (2) develop a pyrite size data bank.

During this quarter, pyrite size analyses of Northern Appalachian Region coal samples continued. Pyrite size analysis has been determined

on eleven different coal samples from the Pittsburgh seam crushed to 14-mesh top size. In addition to the pyrite size analyses, maceral analyses are being performed on the raw, float 1.40 specific gravity fraction and sink 1.40 specific gravity fraction of these samples. Also, degree of association of pyrite particles with coal is being determined. Similar analyses are being performed on samples crushed to 325-mesh top size.

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 chemically desulfurize coal. 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 various 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.

One approach to this problem involves the study of the reactions of high molecular weight organosulfur model compounds and polymers with reagents such as alkali metal hydroxides. During this quarter, work continued on the preparation of several sulfur-containing (thiophenic) polymers for use in studying various chemical desulfurization procedures. In addition, these polymers will be calibration standards for the controlled-atmosphere, programmed-temperature apparatus that is being used to analyze for organic sulfur in coal by a direct method. Accurate methods of analyzing for organosulfur groups in coal are necessary prerequisites for studying chemical desulfurization of coal.

During the next quarter, preparation of sulfur-containing model compounds and polymers will continue. In addition, experiments will begin to study the action of strong nucleophiles on coal and model compounds. The efficiency and mode of action for sulfur removal by these reagents will be determined.

Table 11.
Washability Analysis Showing the Effects of
Crushing on the Liberation of Pyritic Sulfur and
Other Impurities for the Waynesburg Coalbed, Monogalia County, West Virginia

Product	Cumulative							
	Recovery, Pct.		Btu/lb	Ash, Pct.	Sulfur, Pct.		lb SO ₂ /MM Btu	
	Weight	Btu			Pyritic	Total		
1½ x 0								
FLOAT	1.30	17.3	20.3	14077	5.3	0.48	1.83	2.6
1.30 - 1.40		58.2	65.0	13433	9.1	1.08	2.27	3.4
1.40 - 1.60		85.8	91.2	12777	13.0	1.33	2.45	3.8
SINK	1.60	100.0	100.0	12019	17.5	1.75	2.76	4.6
¾ x 0								
FLOAT	1.30	18.9	22.4	14205	4.7	0.52	1.49	2.1
1.30 - 1.40		59.1	66.5	13453	9.1	1.00	1.93	2.9
1.40 - 1.60		85.4	91.4	12802	13.1	1.25	1.96	3.1
SINK	1.60	100.0	100.0	11954	18.1	1.83	2.45	4.1
14 x 0								
FLOAT	1.30	22.0	26.0	14302	4.1	0.28	1.43	2.0
1.30 - 1.40		59.6	67.4	13656	7.9	0.59	1.66	2.4
1.40 - 1.60		85.6	92.0	12979	12.0	0.87	1.91	2.9
SINK	1.60	100.0	100.0	12096	17.1	1.70	2.62	4.3
65 x 0								
FLOAT	1.30	27.2	33.2	14547	2.8	0.10	0.99	1.4
1.30 - 1.40		58.0	67.7	13931	6.4	0.21	1.27	1.8
1.40 - 1.60		83.6	91.9	13112	11.3	0.42	1.45	2.2
SINK	1.60	100.0	100.0	11931	18.1	1.63	2.65	4.4
200 x 0								
FLOAT	1.30	25.6	31.3	14522	2.9	0.11	1.10	1.5
1.30 - 1.40		57.8	67.8	13964	6.2	0.20	1.32	1.9
1.40 - 1.60		82.2	91.2	13217	10.7	0.33	1.42	2.1
SINK	1.60	100.0	100.0	11911	18.1	1.51	2.74	4.6
325 x 0								
FLOAT	1.30	26.6	32.4	14463	3.2	0.10	1.21	1.7
1.30 - 1.40		49.6	58.8	14089	5.4	0.10	1.30	1.8
1.40 - 1.60		79.1	89.1	13379	9.7	0.15	1.39	2.1
SINK	1.60	100.0	100.0	11878	18.3	1.70	2.90	4.9

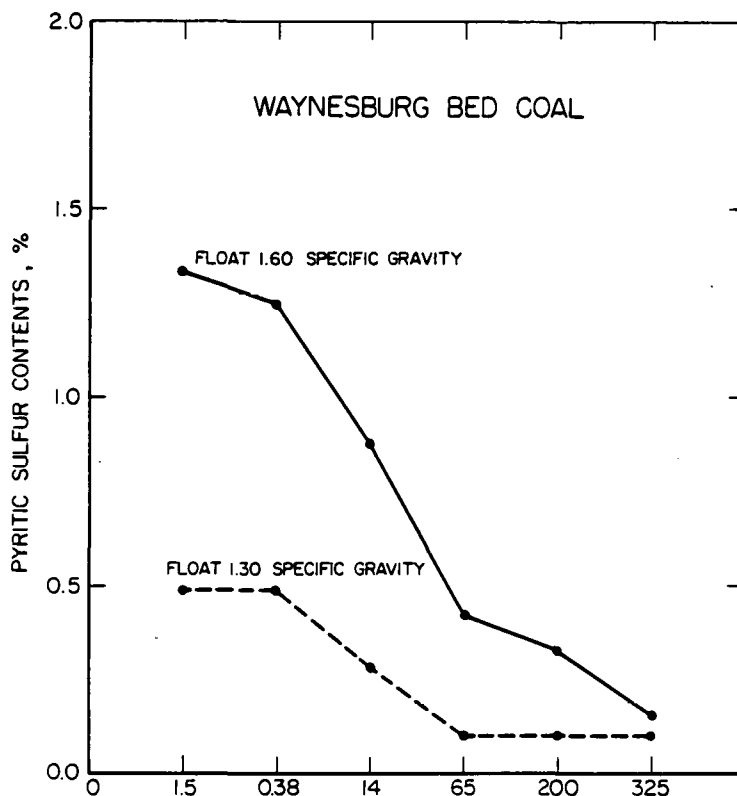


FIGURE 1. TOP SIZE TO WHICH COAL WAS CRUSHED, inches and mesh

Selective Coalescence

R.P. Killmeyer, 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.

The project was initiated this quarter with efforts in three areas: (1) compilation of a bibliography on selective coalescence; (2) procurement of laboratory equipment and supplies; and (3) determination of laboratory test procedures.

All of the references (a few hundred) for the bibliography have been gathered and cross-checked. Most of the references deal with oil agglomeration processes, as there is very little information on some of the newer processes that utilize different agglomerants.

Most of the equipment needed to begin testing was procured, including blenders, rheostats, screens, Freon, heptane, and some coals for preliminary testing. The coals for testing on a long-term basis will be chosen in conjunction with those needed for some of the other in-house coal preparation projects.

Allied to the development of laboratory test procedures, several preliminary test series were run to determine the sensitivity of the results to certain parameters, such as: (1) size of screen to recover coal agglomerates; (2) top size of feed coal; and (3) amount of rinse water for the screening step. From preliminary results, it appears that rinsing time (between 1.5 minutes and 6 minutes) has little effect on the separation. In general, however, finer coal requires finer screens, and finer screens produce more efficient separations in progressing from 28-mesh to 200-mesh screens. This work will continue next quarter. Also, shake-down testing was completed on the new Microtrac particle size analyzer. To gather information on the test procedures of other organizations involved in selective coalescence, research visits were made to the National Research Council of Canada, Otisca Industries, Gulf R&D, TVA, and Battelle.

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 objectives are to develop new or improved fine coal flotation methods to more selectively remove ash and pyritic sulfur from fine coal, and to improve the efficiency of mechanical dewatering of the fine, cleaned product.

During this quarter, coal samples (both run-of-mine and cleaned) were obtained from various coalbeds throughout the U.S. for laboratory flotation work. Also, a 350-pound sample of Bruceston mine coal was obtained for dewatering tests.

The various coals to be used for flotation were crushed to minus 1/2 inch and stored under argon until needed for testing. When needed, each coal was pulverized to either minus 35 mesh or minus 200 mesh and split into representative 200-gram increments.

In a continuing program of flotation tests with low-rank coals, fatty acids, such as oleic acid and tall oil, are being used (along with fuel oil and MIBC when needed) in an effort to improve ash reduction and pyrite rejection. So far only preliminary and inconclusive data are available for this work.

In vacuum filtration tests with a 30% solids slurry of minus 35-mesh Bruceston mine coal (about 20% minus 400-mesh), filter cake moisture content was reduced to less than 13% as a result of the addition of an amine flotation promoter along with a nonionic surfactant prior to filtration. Without the reagents, the moisture content of the filter cake was about 20%. Similar tests with

nominal minus 200-mesh (about 80% minus 400-mesh) coal resulted in final filter cake moisture levels of about 22% as compared to slightly less than 30% without the reagents.

Fine-Size Coal Agglomeration

P.D. Bergman, Cost Account Manager

*A.W. Deurbrouck, Chief,
Coal Preparation Branch*

Previous research had been devoted to employing coal agglomeration methods to extend the economic radius of utilization of lignite and to provide new applications for presently unusable coal fines. The current emphasis of the project is directed at developing cost-effective agglomeration technology for the successful transportation, handling, and storage of deep-cleaned ultrafine coal. The coal pellets formed must be resistant to dusting, weathering, freezing, and spontaneous combustion, and have a low moisture content and high heating value.

This past quarter, a simple closed-system apparatus for preparing a coal-based binder in a controlled, reproducible way was constructed. Using a new binder formulation, coal pellets with acceptable strength and stability characteristics were produced. A satisfactory yield of 70% to 80% usable bituminous coal pellets was obtained by means of water addition to the pelletization mixture. Efforts are underway to duplicate these results and assess experimental uncertainties.

A laboratory furnace has been acquired and installed for the purpose of conducting small-scale exploratory experiments directed at producing a coal-based binder from coals other than lignite. The relationship of binder yield, and physical and chemical characteristics to reaction temperature and heating time will be examined.

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, four attrition tests were conducted on the sorbent used in the fluidized-bed copper oxide process. Attrition rates of the copper oxide sorbent did not exceed 0.05%/hr in the test results analyzed to date. In addition, preparations are being made for a small-scale (35 SCFM to 200 SCFM) continuous fluidized-bed copper oxide process development unit that will be operated to determine the effective life of the sorbent.

Development of an analytical methodology for the analysis of organic constituents in leachates continued this quarter with a meeting of the ASTM Committee on Solid Waste. It was recommended that the "Proposed Method for the Determination of Semi-Volatile Organic Compounds in Aqueous Leachates of Wastes," ASTM document 34.03-010, go to balloting at the Section level and undergo ASTM round-robin testing.

**PETC Combined
Flue Gas Cleanup Support**
R.J. Demski, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch

The objective of this project is to conduct experimental studies in support of the DOE Flue Gas Cleanup Program. Emphasis is placed on parametric evaluation of processes that provide simultaneous removal of SO₂, NO_x, and particulates from the flue gas of coal-fired boilers.

During this quarter, four 100-hour copper oxide attrition tests were conducted in the 40" x 48" fluidized bed in the flue gas stream of the PETC 500 lb/hr Solid-Fuel Combustion Test Facility. These tests measured the effects of flue gas temperature, thermal cycling, and sulfur dioxide absorption on the attrition of the copper oxide sorbent. Results analyzed thus far indicate attrition rates of no more than 0.05%/hr, which are comparable to earlier results obtained from a PDU reactor and a 9½-in.-i.d. plastic model.

Additional testing completed on the 500 lb/hr Solid-Fuel Combustion Test Facility were baseline and spray dryer/ESP SO₂ removal tests for a low-sulfur bituminous coal. These tests were performed in cooperation with Wheelabrator-Frye, Inc.

All other efforts in this project were initiated this quarter. Facilities for these efforts are currently in the design stage, with flow sheets being prepared.

A. Proof-of-Concept Testing

During FY83, a project involving simultaneous removal of SO₂ and 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 will be made to

identify the causes of sorbent attrition, and approaches to correcting the problem will be identified. The tests will be conducted in the PETC 500 lb/hr Solid-Fuel Combustion Test Facility. Interwoven with these tests will be three short series of spray dryer/ESP tests conducted in cooperation with Wheelabrator-Frye, Inc.

Upon completion of copper oxide process tests in FY84, exploratory tests will be initiated involving combined SO₂/NO_x removal from flue gas via spray dryer injection of sodium/aluminum based sorbents.

During this reporting period, two 100-hour copper oxide attrition tests were conducted in the 40" x 48" fluidized bed, one at ambient temperature and the other at 750°F while burning natural gas. The gas velocities for the ambient-temperature test were 117 ft/sec at the exit of each bubble cap and 2.9 ft/sec in the bed, while at 750°F the velocities were 168 ft/sec and 4.2 ft/sec, respectively.

Table 12 lists the data from these two tests. The hourly attrition rates during both tests were comparable to results obtained earlier in the PDU reactor and during ambient-temperature tests in a 9 1/2-in.-i.d. plastic model.

Another series of 100-hour attrition tests has been completed. In the first test (ATT-3), natural gas was burned to produce a 750°F bed temperature, and ambient-temperature sorbent was fed into the bed at a rate of 200 lb/hr to study the effect of thermal cycling on attrition. Natural gas was also burned in the next test; however, in this test the reactor was charged with 800 lb of sorbent before initiating combustion, and there was no addition or withdrawal of sorbent during the test. Sulfur dioxide was added to the flue gas to sulfate the sorbent. Results of these tests are being analyzed.

During the next quarter, another batch attrition test will be completed in the 40" x 48" fluidized bed using SO₂/NO_x/NH₃ injection while burning natural gas. Also, an attrition test will be conducted in the 9 1/2-in.-i.d. plastic model using ambient-temperature air while injecting fly ash.

In cooperation with Wheelabrator-Frye, Inc. (WFI), baseline and spray dryer/ESP tests have been completed on a low-sulfur bituminous coal at SO₂ removal rates of 70%, 80%, and 90%. The particulate collected in the ESP has been blended in preparation for recycle tests to

Table 12.
100-Hour Sorbent Attrition Tests
Batch Operation, 40" x 48" Fluidized-Bed Reactor

	Ambient- Temperature Air	750°F Natural Gas Combustion Products
1. Sorbent Charged, lb	808.8	784.8
2. V_g at Bubble Cap Exit, ft/sec	117	168
3. V_g In Bed, ft/sec	2.9	4.2
4. Fines (-20 Mesh) In Discharged Sorbent, lb	10.7	8.6
5. Carry-over Collected In Baghouse, lb	30.4	28.6
6. Sieve Analysis/Copper Concentration of Carry-over, %		
>40 Mesh	3.6/1.4	12.9/2.7
40-100 Mesh	14.9/2.8	20.0/3.3
100-200 Mesh	12.9/2.5	27.7/3.1
200-325 Mesh	14.9/2.1	14.7/3.1
<325 Mesh	53.6/2.3	24.5/2.3
6. Attrition, %/hr $\left(\frac{\text{Item 4} + \text{Item 5}}{\text{Item 1}} \right)$	0.05	0.04

be completed in January 1984. The particulate collection results obtained to date indicate that EPA particulate standards can be achieved.

B. Supporting Activities

1. Copper Oxide Process, Continuous Life-Cycle Tests

Along with the attrition testing in the 500 lb/hr Solid-Fuel Combustion Test Facility, a small-scale (35-200 SCFM) continuous PDU will be constructed and operated 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 a 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.

Personnel for this project became available in December. An area has been made available for the construction of the small-scale continuous PDU. Two power plants and the PETC steam plant were visited to investigate the possibility of installing the PDU on a slipstream from one of these existing coal-fired facilities.

A preliminary flow sheet is being prepared by GE/Matsco, the combustion facilities operating contractor, for DOE's approval. Preliminary vessel sizes and materials of construction will be included in the first flow sheet. A detailed flow sheet will be completed in January.

2. Dry Combined Flue Gas Cleanup Processes

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 or sorbent combinations with potential for combined SO₂/NO_x removal. Exploratory tests will be conducted in an existing laboratory PDU that will be equipped with a small spray dryer (30-inch-diameter) and a fabric filter. The candidate sorbents will be evaluated as dry powders injected into the flue gas ducting and as solutions/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.

Personnel for this project became available in December. The existing flow sheet of the PDU is being redrawn to include the desired changes for this new project. One of the major changes is the design of a new furnace that can be operated with a much shorter start-up time than the existing furnace.

Modifications to the existing equipment have already begun. After final approval of a flow sheet, construction of the new furnace and other process components will begin. Construction is expected to be completed by the end of the next quarter.

3. Combined Flue Gas Cleanup With Metal Oxides and Reducing Gases

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 will be used for this purpose. A laboratory-scale apparatus will be constructed to evaluate the catalytic activity of the metal oxides and sulfates in decomposing NO_x using 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 will be undertaken using unsupported copper oxide. Previous tests done by DeBerry and Sladek¹ for SO₂ reactions with metal oxides showed that copper oxide (CuO) had the highest reaction rate with SO₂ for temperatures above 400°C of all metal oxides tested. Fluidized-bed tests have been performed on the PETC 500 lb/hr Solid-Fuel Combustion Test Facility in which copper oxide was supported on 1/16-inch-diameter gamma alumina spheres. Results showed that SO₂ readily reacts with copper oxide in this environment; furthermore, both copper oxide and copper sulfate act as catalysts to reduce NO_x when ammonia is injected into the flue gas prior to the fluidized bed. Simultaneous removal of 90% of both SO₂ and NO_x were obtained from a flue gas containing 3100 ppm SO₂ and 520 ppm NO_x.² Testing of copper oxide will take advantage of the experience drawn from fluidized-bed tests, microbalance tests, and

References

1. DeBerry, D.W., and Sladek, K.J., "Rates of Reaction of SO₂ with Metal Oxides," *The Canadian Journal of Chemical Engineering*, Vol. 49, pp. 781-785, Dec. 1971.
2. Demski, R.J., Yeh, J.T., and Joubert, J.I., "Experimental Evaluation of Advanced Flue Gas Cleanup Processes." Presented at the Fifth Annual Symposium on Industrial Coal Utilization, Pittsburgh, Pa., June 6-7, 1983.

previous tests of copper oxide performed on smaller-scale units, but the use of copper oxide powder will avoid the costs of the alumina support used in the fluidized-bed process.

Design of the laboratory-scale packed-bed reactor has been initiated. Due to the temperatures that may be necessary to thermally regenerate the sorbents, and to avoid the possible interfering effects of other materials, such as steel, the reactor will consist of a 1-inch-diameter quartz tube fitted with a quartz fritted disk. The reactor will be operated with a downflow of gas, enabling the bed depth to be easily varied so that studies may be made with both a deep bed or differential bed of sorbent. A mass spectrometer is being considered for use as the principal gas analyzer. However, other analyzers will be necessary to measure NO_x , COS , and water vapor in the off-gas.

In the next quarter, microbalance tests will be initiated to measure the kinetics of SO_2 absorption by copper oxide powder. The copper oxide powder used for testing will be both technical grade copper oxide and thermally regenerated copper sulfate pentahydrate.

4. Advanced Separation Techniques for Application to SO_2/NO_x Cleanup Processes

The objective of this project is to evaluate potential applications for advanced separation techniques in flue gas cleanup processes. Advanced separation methods include membrane separations, supercritical extraction, liquid-liquid extraction, ion exchange, resin adsorption, and electrophoresis. Flue gas cleanup processes to be examined include those using absorption/regeneration cycles for combined SO_2/NO_x removal.

Detailed work plans have been prepared for this activity. The evaluation of advanced separation processes will be conducted largely through a review of the literature, access to other available information on advanced separation techniques and flue gas cleanup processes, and an engineering assessment of the potential for applying these techniques to applications related to SO_2/NO_x control.

A preliminary literature survey on advanced separation techniques has been con-

ducted. Experts in membrane separation techniques have been contacted. A review of absorption/stripping processes for SO_2/NO_x removal is underway.

5. Lurie Process Evaluation

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 SO_2 and NO_x absorption by a series of measurements of vapor pressures over the sodium aluminate slurry as a function of concentrations, temperatures, and slurry pH.

Detailed work plans were prepared. These primarily describe what is necessary to get the experimental rig ready for the required measurements of vapor pressures over the (sodium aluminate slurry) absorbent used in the Lurie Process.

A two-chambered counterflow absorber has been fabricated to give a long exposure time of the absorbent to the absorbing medium (in the tube connecting the two chambers) while not requiring an excessive amount of absorbent (approximately 700 mL of slurry). The first task is to shake down this apparatus.

The second task will be to examine the role certain process variables or additives have on SO_2 and NO_x removal. This will be done in the following manner:

- (a) Select an "always pumpable" absorbent concentration. Several concentrations of NaAlO_2 solutions will be neutralized with 10 wt% H_2SO_4 to gain familiarity with the properties of the floc, and to find a concentration that gives a reasonable prospect of pumpability. A concentration will be called "always pumpable" if it remains pumpable throughout the pH range from that for the freshly prepared NaAlO_2 (around pH 12) down into the acid range characterized by enough excess H_2SO_4 to dissolve the floc.
- (b) Titrate a sample of the "always pumpable" concentration with H_2SO_4 . These experiments are to be run at 40°C, 50°C, and 60°C. We expect to observe a long plateau of constant pH along an interval of acid addition, along which the floc will be observed to further dissolve in added

acid, but that does not lead to any net change in pH after each acid addition is well mixed and the temperature has been allowed to return to the target temperature. We expect that complete dissolution of the floc will occur only when the pH is below 3.0. This relatively simple experiment will give good experience in use of pH meters.

- (c) Establish the concentration of SO₂ that equilibrates with a slurry whose pH can be held constant (buffered) by the presence of the alumina floc. For this purpose, the counterflow absorber constructed and tested in the first task will be used.
- (d) Evaluate the effects of various oxidation catalysts on production of sulfate ion in aqueous medium from SO₂ gas. It will be necessary to repeat the adjusted pH runs above with ferric sulfate present in the absorbent medium as well as to repeat the pH and SO₂ vapor pressure runs (P_{SO₂}) in the alkaline range.
- (e) Evaluate the effect of NO on SO₂ absorption by performing runs with NO present at 1000 ppm in the artificial flue gas and by repeating the adjusted pH runs above and the pH and P_{SO₂} runs in the alkaline range.
- (f) Evaluate the effect of acid medium (acid sulfate) on NO oxidation and absorption by repeating the adjusted pH runs above with ferric sulfate present in the absorbent medium and with NO present at 1000 ppm in the artificial flue gas.

The third task will be to assess process chemistry required for a continuous system with high SO₂ removal and, using a mathematical model as necessary, to estimate any costs due to pressurization of medium in moving from one chamber to the other.

**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, the ASTM Committee on Solid Waste met in Denver, Colo., and the Section responsible for the previously developed analytical method recommended that it go to balloting at the Section level and undergo ASTM round-robin testing at the same time. Therefore, final comments and corrections were incorporated into the "Proposed Method for the Determination of Semi-Volatile Organic Compounds In Aqueous Leachates of Wastes," ASTM document 34.03-010. The document was sent to ASTM Headquarters for duplication and distribution. The Section-level balloting is important because it represents the first opportunity for Section-level members to officially comment on the analytical method. Additionally, Section-level balloting represents the first step of formal acceptance of the analytical method as a standard.

A protocol for the ASTM round-robin testing of the method was formulated at the Denver meeting in conjunction with the Chairman of ASTM Committee E-11 on Statistics. Current plans call for testing the analytical method at three concentration levels (the original leachate and two dilutions). The aqueous leachate that will be analyzed during the round robin was sent to Ames Laboratory from EPA. At Ames, the leachate is being filtered to remove solids and composited in a large container for homogenization. This container is wrapped in Al foil and stored at 4°C until it is shipped to the volunteer labs for round-robin analysis.

Before the aqueous leachate is sent to the volunteer labs, a considerable amount of analytical work must be performed. Both Ames and PETC have extracted a liter of the waste and have analyzed it by combined GC-MS and by ultra-

high resolution mass spectrometry. Fourteen organic compounds have been identified tentatively using these techniques at PETC. Analytical reference standards of many of the analytes tentatively identified in the waste leachate are being purchased. Acquisition of these standards is necessary because (1) they will permit verification of previously made tentative identifications, and (2) they will allow us to analyze the leachate that will undergo round-robin analysis using the analytical method. Before the planned ASTM round robin can begin, the aqueous leachate and its dilutions must be analyzed by the analytical method to insure that the method works well on this sample. Once the

sample is thoroughly analyzed using the analytical method, and we are confident that the method works well on the sample and its dilutions, it will be sent to the volunteer labs.

The first draft of a report describing the results of analysis of H-Coal filter cake leachates by the previously developed analytical method was prepared. The document is entitled "Limited Round-Robin Investigation of an Analytical Method for the Determination of Semi-Volatile Organics in Aqueous Leachates of Solid Wastes: Application to H-Coal Filter Cake Leachates." This draft was distributed to the co-authors for their 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 utilizing 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) fire-tube 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, analysis of the results from the combustion tests conducted in the 700-hp boiler with coal-methanol-water (CMW) mixtures were completed. The results from CMW tests conducted with a high volatile A (hvA) bituminous coal and a high volatile C (hvC) bituminous coal showed that the lower rank hvC bituminous coal burned more efficiently under the same conditions to give higher carbon conversions (all better than 99.5%). Combustion test results with micronized CWMs indicated a carbon conversion efficiency of 98% using a coal particle size-consist of 87% minus 19 microns compared to a

carbon conversion efficiency of 96% using a coal particle size-consist of 90% minus 74 microns (200 mesh). During combustion tests with a commercial CWM using combustion air enriched to 23% oxygen, the air preheat temperature was reduced to 200°F as compared to 370°F required with no oxygen enrichment. Two viscosity-reducing additives, Fiosperse and Dispersant A-23, were evaluated in the fuel rheology laboratory. The Fiosperse additive (manufactured by Pfizer) was ineffective in this experiment, while the Dispersant A-23 (manufactured by Diamond Shamrock) was an effective viscosity reducer when slurry pH was kept slightly elevated.

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 utilizing coal-water mixture (CWM) fuels in industrial boilers designed to burn fuel oil. During this quarter, analysis of the results from the combustion tests conducted with coal-methanol-water (CMW) mixtures was completed. The CMW tests were conducted with a high volatile A (hvA) bituminous coal and a high volatile C (hvC) bituminous coal to determine the minimum level of methanol required in the fuel mixture to maintain a stable flame without preheated combustion air and to compare boiler performance when using the different fuels. The test program to study the effect of coal particle

size-consist on combustion properties of CWM was also continued. Oxygen-enrichment tests were also conducted during this quarter to determine the minimum oxygen concentration required to stabilize the CWM flame without preheating the combustion air and to evaluate other associated beneficial effects on boiler performance.

With CMW mixtures containing 60% hvA bituminous coal, the minimum level of methanol required without using preheated combustion air was determined to be about 16%. The carbon conversion and boiler efficiencies at full load for the mixtures containing 12% to 39% methanol were in the ranges of 92% to 98% and 72% to 81%, respectively, when the combustion air temperature varied from ambient temperature to 500°F. Preliminary results are summarized in Table 13.

With CMW mixtures containing hvC bituminous coal, no more than 51% coal could be added because of the formation of high viscosity mixtures resulting in high fuel pump pressure and nozzle-plugging problems. A series of combustion tests with mixtures containing 51% coal showed that CMW mixtures containing 23% or less methanol required preheating of the combustion air to be fired successfully. For mixtures containing 12% to 45% methanol, the carbon conversion efficiencies at full load were all better than 99.5%, and the boiler efficiencies were in the range of 76% to 82% when the combustion air temperature was varied from ambient temperature to 500°F. Preliminary results are summarized in Table 14.

The presence of methanol in a coal-water mixture promotes flame stability and increases carbon conversion and boiler efficiencies. In comparison with the CMW mixture prepared with hvA bituminous coal, the CMW mixture prepared with the lower-rank hvC bituminous coal burned more efficiently under the same conditions to give higher carbon conversions.

Coal particle-size tests were conducted with a CWM prepared with a beneficiated Eastern Kentucky coal containing 2% ash. A test was conducted with a CWM containing 58% coal having a particle size-consist of 87% minus 19 microns. At full boiler load, a carbon conversion efficiency of 98% was obtained when using 500°F combustion air. This is a slight improvement over the 96% carbon conversion efficiency obtained previously with a CWM containing 62% coal having a particle size-consist of 90% minus 74 microns (200 mesh). It was also noticed that the rate of ash deposition in the furnace was considerably reduced during the micronized CWM combustion test.

During this quarter, the test series to study the effects of the use of oxygen-enriched air on CWM combustion was concluded. A commercial grade CWM fuel, produced by the Atlantic Research Corporation, was used. The CWM fuel consisted of 71% coal, 28% water, and 1% additive. Initial tests were conducted to evaluate different oxygen injection methods by introducing oxygen down either (1) the center air stream or (2) the burner guide tube. Each test involved initially setting the boiler at full-load conditions without oxygen-enrichment using 15% excess air at 370°F pre-heat. Oxygen was then injected at a rate equivalent to enriching the overall oxygen concentration to 23%. A constant 15% excess oxygen to fuel ratio was maintained by adjusting the secondary air flow rate. The minimum combustion air preheat temperature required at the 23% oxygen-enrichment level was then determined by slowly reducing the combustion air preheat temperature until the CWM flame reached borderline stability. Prior to formal testing, various configurations of center air swirlers and guide tube diffusers were tested to select the best burner arrangement. When using this burner configuration, it was determined that the minimum combustion air preheat temperature at 23% oxygen enrichment was about 200°F for both oxygen injection methods. Data are being analyzed to determine the effect of oxygen enrichment on heat release, combustion rate, and boiler performance.

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 fuels to replace fuel oil firing in conventional combustion equipment and to evaluate unique retrofit burners. 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, the coal-water mixture (CWM) particle size tests were continued in the 100-hp Combustion Test Facility. Tests were also initiated to study the effect of ash content on combustion properties of CWM prepared with micronized coals. Eastern Kentucky coal having a particle size-consist of 90% minus 20 microns and beneficiated to different levels of ash content

Table 13.**Combustion Tests of CMW Mixtures Prepared with High Volatile A Bituminous Coal**

Fuel Composition, %							
Dry Coal	59.9	59.9	59.4	59.4	59.8	60.3	
Methanol	15.8	15.8	19.8	19.8	23.8	23.8	
Water	24.3	24.3	20.8	20.8	16.4	15.9	
Heating Value, Btu/lb	9,411	9,411	9,642	9,642	10,170	10,295	
Boiler Load	Full	Half	Full	Half	Full	Half	
Combustion Air Temperature, °F	119	389	102	346	72	299	
Excess Air, %	7	17	10	20	12	14	
Steam Flow, lb/hr	23,230	12,600	26,520	11,820	25,890	12,170	
Carbon Conversion, %	93.5	97.4	91.6	97.1	94.8	96.5	
Boiler Efficiency, %	74.8	79.2	71.6	78.5	75.2	8.14	

Table 14.**Combustion Tests of CMW Mixtures Prepared with High Volatile C Bituminous Coal**

Fuel Composition, %							
Dry Coal	50.1	50.1	50.3	50.5	50.5	51.6	50.9
Methanol	12.4	12.4	22.8	36.6	36.6	44.6	45.4
Water	37.5	37.5	26.9	12.9	12.9	3.8	3.7
Heating Value, Btu/lb	6,881	6,881	7,949	9,213	9,213	10,326	10,190
Boiler Load	Full	5/8*	Full	Full	Half	Full	Half
Combustion Air Temperature, °F	300**	508	188**	88	504	104	167**
Excess Air, %	17.0	16.3	16.8	17.6	16.2	16.6	17.9
Steam Flow, lb/hr	23,290	14,980	23,780	23,570	12,620	23,860	12,440
Carbon Conversion, %	99.4	99.8	99.5	99.8	99.9	99.8	99.9
Boiler Efficiency, %	75.5	78.4	75.7	77.6	81.5	78.9	81.3

*Minimum boiler load based on stable combustion and carbon monoxide emissions ≤ 400 ppm.

**Minimum combustion air preheat based on stable combustion and carbon monoxide emissions ≤ 400 ppm.

has been used. The Peabody CWM burner with six 0.159-inch nozzle orifices was used in the tests. Preliminary results indicate that the use of beneficiated coal offers improvements in CWM combustion.

Combustion tests conducted with the CWM containing 61% micronized coal beneficiated to 2.5% ash content showed that the CWM fuel could be burned successfully at full boiler load (3450 lb/hr steam output) with ambient-temperature combustion air. Fuel pressures were about 60 psig at the burner and remained very stable throughout tests. The excess air level was 10%, and flue-gas oxygen levels and carbon monoxide emissions averaged 3.3% and 180 ppm, respectively. A 91.6% carbon conversion and 73.6% boiler efficiency were achieved. A test with the same CWM but using 62.4% coal loading and 300°F combustion air showed a small improvement in carbon conversion and boiler efficiencies (92.9% and 74.8%, respectively) at 18% excess air level. Preliminary results are summarized in Table 15.

In tests with the CWM containing 61% coal beneficiated to 7.8% ash, this CWM could not be burned with ambient-temperature combustion air but required combustion air preheated to 316°F. A carbon conversion of 84.9% and a boiler efficiency of 68.5% were obtained (see Table 15). It appears that the higher ash content and the lower heating value of this CWM caused the decrease in both carbon conversion and boiler efficiencies.

With a CWM prepared from the same parent coal containing 10.3% ash and micronized to a particle size-consist of 90% minus 19 microns, the requirement for combustion air preheat further increased. At a 61% coal loading, this CWM fuel could not be fired without combustion air preheated to 500°F. The combustion was also plagued with severe slag formation around the flame oven cone, and ash deposition on the fire-tube floor.

Fuel Rheology Laboratory
A.C. Ekman, Cost Account Manager
J.I. Joubert, Chief,
Combustion Technology Branch

The experimental coal storage system has been rebuilt to incorporate a larger storage vessel, and a new test has begun. The sample coal is being agitated under nitrogen during storage, and the properties of slurries prepared periodically from this sample will be compared to those of slurries prepared from coals exposed to air. Previous tests using a smaller storage vessel were inconclusive; and it is hoped that an increased test duration, made possible by the larger sample, will increase the significance of the results.

Tests are being continued that will evaluate in greater detail the capabilities of the Micromeritics Zeta Potential Analyzer. Electrophoretic mobilities are being measured in slurries over several concentrations and additive levels.

Table 15.
Combustion Tests of CWM Prepared with Beneficiated Eastern Kentucky Coal

Fuel Composition, %					
Dry Coal	61.0	61.0	62.4	60.9	61.0
Water	39.0	39.0	37.6	39.1	39.0
Heating Value, Btu/lb	8,935	8,935	9,235	9,013	8,532
Ash in Coal, %	3.3	3.3	2.5	2.5	7.8
Particle Size-Consist of Coal	96% <74 μ	96% <74 μ	89% <19 μ	90% <19 μ	91% <19 μ
Combustion Air Temperature, °F	528	95	300	94	316
Excess Air, %	14	12	18	10	11
Steam Flow, lb/hr	3,457	3,457	3,386	3,533	3,406
Carbon Conversion, %	92.9	91.4	92.9	91.6	84.9
Boiler Efficiency, %	75.3	72.1	74.8	73.6	68.5

Several combinations of instrument settings will also be evaluated. Viscosity measurements are being made on the same slurries, and data will be compared.

A series of viscometric evaluations was performed on slurries prepared in the laboratory using Kentucky "7% Ash" coal. The coal was pulverized to several size distributions in the combustion test facility. Coal concentrations and shear rates were specified by the test facility engineers; additive concentrations were varied by the laboratory technicians, who tried to produce, for each size distribution, slurries with viscosities

below 500 cp. Technicians also observed and reported any tendency for these slurries to thicken in response to time or to increased shear, since this is a serious handling problem. Size distributions were measured using the Microtrac, and the percentages less than 75 μm (200 mesh) and 19 μm were reported. Viscosities were measured using the Haake Rotovisco at constant rates (100, 400, 700, and 1000 sec^{-1}) over two-minute periods; measurements made after 50 seconds and after 100 seconds were reported. Measurements were made at room temperature. The coarsest of these coals (see Table 16 for

Table 16.
Viscosities of Coal-Water Slurries

Virginia "7% Ash" Coal pulverized in Sweco Mill at Combustion Test Facility				
Size distribution: 88.7% less than 75 μm				
58.0% less than 19 μm				
Coal Concentration, (wt%)	Additive Dose (wt%)*	Viscosity After 50 sec (cp)	Viscosity After 100 sec (cp)	Shear Rate (sec^{-1})
60.0	None	339	310	100
		170	158	400
		150	138	700
		132	117	1000
62.5	None	841	796	100
		386	350	400
		280	253	700
		263	234	1000
62.5	0.25	151	142	100
		195	177	400
		195	175	700
		171	155	1000
62.5	0.50	147	130	100
		177	158	400
		160	145	700
		164	144	1000
65.0	0.50	354	324	100
		361	310	400
		312	269	700
		283	245	1000

* Percent Lomar D viscosity reducer in entire slurry.

Table 17.
Viscosities of Coal-Water Slurries

Virginia "7% Ash" Coal pulverized in Sweco Mill at Combustion Test Facility				
Size distribution: 99.5% less than 75 μm				
90.0% less than 19 μm				
Coal Concentration, (wt%)	Additive Dose (wt%)*	Viscosity After 50 sec (cp)	Viscosity After 100 sec (cp)	Shear Rate (sec ⁻¹)
60.0	0.25	413	407	100
		282	292	400
		274	290	700
		268	283	1000
62.5	0.50	767	752	100
		1053	1053	400
		---	---	700
		---	---	1000
62.5	0.75	413	383	100
		523	494	400
		552	478	700
		549	442	1000

*Percent Lomar D viscosity reducer in entire slurry.

selected data) produced acceptable slurries in all of the combinations tested; the slurries prepared without viscosity-reducing additive had high viscosities at 100 sec⁻¹ but became much less viscous in response to increasing shear. The slurries prepared from the most finely ground coal were less fluid, but the addition of Lomar D additive decreased viscosity acceptably (see Table 17). The 62.5% slurries were both shear-thickening, however, even when viscosity was reduced to around 500 cp. A 7% ash coal of intermediate size was evaluated in a few mixes requested specifically by test facility engineers (see Table 18). All of the combinations evaluated were fluid enough to be used, although the 62.5% slurry was shear-thickening. These data were given to the engineers who are planning the micronized-coal combustion tests.

A slurry prepared at the combustion test facility with approximately 59% micropulverized "2% ash" coal and an unspecified dosage of Lomar D was evaluated viscometrically over a range of temperatures requested by test facility engineers.

Some of the tests were repeated after the concentration was increased by evaporation. Viscosities decreased overall as a function of temperature, although dilatancy (the tendency to thicken with increased shear) appeared to increase after heating (see Table 19). Low shear viscosities in the second set of tests were lower than the first set even though coal concentrations were higher. The reason for this is not clear. Small increases in concentration or changes in the characteristics of the additive might explain the increased dilatancy, which is a severe problem in coal slurries; high viscosities at high rates of shear can prevent good atomization. Test facility operators who tried to reduce their problems with this slurry by adding extra Lomar D found themselves instead with a sticky, intractable mess; excess additive can cause problems as severe as insufficient additive. Further experimentation with micronized coal and the viscosity-reducing additives is necessary for the preparation of an optimum fuel. The effects of temperature on fuel characteristics should also be further examined.

Table 18.
Viscosities of Coal-Water Slurries

Virginia "7% Ash" Coal pulverized in Sweco Mill at Combustion Test Facility Size distribution: 99.1% less than 75 μ m 65.0% less than 19 μ m				
Coal Concentration, (wt%)	Additive Dose (wt%)*	Viscosity After 50 sec (cp)	Viscosity After 100 sec (cp)	Shear Rate (sec ⁻¹)
60.0	None	802	779	100
		406	383	400
		295	275	700
		252	233	1000
62.5	0.50	130	124	100
		140	130	400
		140	131	700
		134	124	1000
62.5	0.75	180	130	100
		168	168	400
		190	173	700
		183	165	1000

*Percent Lomar D viscosity reducer in entire slurry.

Table 19.
Viscosities of a Coal-Water Slurry Over a Range of Temperatures

Slurry prepared at combustion facility using 2% ash coal and Lomar D.				
Temperature	Viscosity* at			Measured Concentration**
	100 sec ⁻¹	200 sec ⁻¹	700 sec ⁻¹	
120°F	148 cp	---	160 cp	58.9%
140°F	131 cp	123 cp	152 cp	58.9%
160°F	105 cp	128 cp	150 cp	58.9%
180°F	115 cp	216 cp	349 cp	59.8%
Concentration increased by evaporation.				
140°F	88 cp	206 cp	350 cp	61.4%
160°F	112 cp	138 cp	278 cp	61.4%
180°F	103 cp	107 cp	273 cp	61.4%

*Viscosities measured after 50 seconds of shear.

**Concentration are weight percents.

Table 20.
Viscosities of Coal-Water Slurries Containing Flosperse Additives
(Compared to Viscosity of Slurries Containing No Additives or Lomar D)

Slurry ^a Composition	Viscosity ^b at 200 sec ⁻¹	pH
60% Coal	885 cp	3.30
60% Coal 0.3% Lomar D	354 cp	3.45
60% Coal 0.3% Flosperse 0.15% Flocon Stabilizer	785 cp	8.95 ^c
60% Coal 0.3% Flosperse 0.15% Flocon Stabilizer	856 cp	3.30
60% Coal 0.3% Flosperse	798 cp	3.30

^aPittsburgh seam coal, 91% through 200 mesh, mixed with tap water.

^bViscosities measured after 50 seconds of shear.

^cpH adjusted with NaOH.

Two viscosity-reducing additives were evaluated. A sample of the first additive, Flosperse (manufactured by Pfizer), was ineffective in this experiment under all of the conditions tested (see Table 20), although viscosity data sent with the sample from Pfizer indicated that the additive was more effective and much less sensitive to dosage level than were polynaphthalene sulfonates (like Lomar D). The second additive, manufactured by Diamond Shamrock and based on Lomar D, contains an ammonium ion in place of Lomar D's sodium ion. This additive, Dispersant A-23, was an effective viscosity reducer when slurry pH was kept slightly elevated. This had been observed in tests with Pittsburgh seam coal carried out during the summer of 1982, and in

tests this quarter with Kentucky "7% ash" coal (see Table 21), and "2% ash" coal (see Table 22). It was observed that these slurries became unstable and nonhomogeneous after heating, and that increasing the additive dosage exacerbated this instability. Problems developed at the combustion test facility when an unstable "2% ash" feed slurry could not be processed through the micropulverizer. The addition of a heated cornstarch solution was tested in the laboratory as an emergency stabilizer, and 0.04% starch was added successfully at the test facility.

Tests are being carried out in the laboratory to provide similar information about Kentucky "10% ash" coal slurries and A-23.

Table 21.
Viscosities of Coal-Water Slurries Containing Dispersant A-23

Kentucky 7% Ash Coal, Standard Grind (88.7% through 75 μm) in tap water		
Slurry Composition	Viscosity at 100 sec⁻¹	Viscosity at 700 sec⁻¹
60% Coal	339 cp	150 cp
60% Coal 0.25% A-23	186 cp	110 cp

Kentucky 7% Ash Coal, Micropulverized (100% through 75 μm, 84% through 19 μm) in tap water		
Slurry Composition	Viscosity at 100 sec⁻¹	Viscosity at 700 sec⁻¹
60% Coal 0.25% A-23	2032 cp	— ^a
60.0% Coal 0.50% A-23	369 cp	761 cp
60.0% Coal 0.50% A-23 0.05% NH ₄ OH	124 cp	472 cp
62.5% Coal 0.75% A-23 0.05% NH ₄ OH	1100 cp	—
62.5% Coal 0.75% A-23 0.16% NH ₄ OH	236 cp	573 cp
62.5% Coal 0.75% A-23 0.40% NH ₄ OH	273 cp ^b	403 cp

Note: Viscosities measured after 50 seconds of shear.

^aViscosity >> 2000 cp.

^bViscosity measured at 200 sec⁻¹ instead of 100 sec⁻¹.

Table 22.
Viscosities of Coal-Water Slurries Containing Dispersant A-23

Kentucky 2% Ash Coal, Standard Grind (~90% through 75 μ m) in tap water		
Slurry Composition (wt%)	Test Temperature (°C)	Viscosity after 50 seconds at Indicated shear rate (cp)
62.5% Coal 0.50 % A-23 (pH 7.24)	40	1711 @ 100 sec ⁻¹
		1682 @ 200 sec ⁻¹
62.5% Coal 0.50% A-23 0.05% NH ₄ OH (pH 8.24)	40	354 @ 200 sec ⁻¹
		368 @ 400 sec ⁻¹
62.5% Coal 0.50% A-23 (pH 7.31)	65	479 @ 200 sec ⁻¹
		1106 @ 400 sec ⁻¹
62.5% Coal 0.50% A-23 0.05% NH ₄ OH (pH 8.14)	65	214 @ 200 sec ^{-1*}
		496 @ 400 sec ⁻¹
		438 @ 700 sec ⁻¹
62.5% 0.75% A-23 0.05% NH ₄ OH (pH 7.95)	65	221 @ 400 sec ^{-1**}
		282 @ 700 sec ⁻¹

*Data are composite of two tests.

**Although the higher A-23 dosage for this sample decreased viscosity, the slurry became grossly unstable.

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 hydro-processing 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.

During this quarter, the capillary tube viscometer that was developed during a previous project was used to measure viscosities of a heat transfer fluid and a coal-derived liquid at ambient temperature and at pressures ranging from at-

mospheric to 2000 psig under both helium and nitrogen atmospheres. These results will indicate the effect of pressure and gas solubility on liquid viscosity. The unit is currently being modified for use at high temperatures and pressures with coal/oil slurries.

Wilsonville vacuum bottoms from Run 242 were fractionated in the Fractional Distraction Unit at a reduced temperature of 1.01 using pentane, cyclohexane, and toluene. Overhead recoveries ranged from 18% to 62%, indicating that the depth of extraction can be controlled by appropriate choice of solvent.

A series of Ni-Mo/Al₂O₃ catalysts having a constant metals loading but different Ni/Mo ratios was prepared and evaluated. Hydrogenation, denitrogenation, and cyclohexane-insoluble conversion activities showed a slight increase up to Ni/Mo = 0.5; desulfurization activity showed more pronounced changes. Coke formation was relatively unaffected. A similar series of experiments is also being performed for Ni-W/Al₂O₃ catalysts.

The addition of a small amount of hydrogen sulfide to the hydroprocessing reactor enhanced catalyst activity for denitrogenation and desulfurization, but not for hydrogenation. The sulfur content of the spent catalyst was also higher for the run with hydrogen sulfide addition compared to the run without. In a companion study, the sulfur content of the catalyst was increased by increasing the sulfiding temperature; however, no differences in activity were observed. The data appear to indicate that the catalyst may reach an equilibrium sulfur content based on the concentration of hydrogen sulfide dissolved in the liquid phase during processing.

The new SRC/solvent feedstock from Wilsonville was evaluated thermally and catalytically in the continuous-flow hydrotreater. At both 720°F and 750°F, the feedstock showed that almost no reactions occur thermally; however, substantial conversions were observed at these temperatures using a PETC-prepared Ni-W/Al₂O₃ catalyst.

A catalyst sample from Wilsonville Run 243 was used to evaluate the performance of various solvents in preparing spent catalysts for further analysis. Samples extracted with cyclohexane, ethyl acetate, tetrahydrofuran, and pyridine showed only minor differences in batch activity tests. Pyridine removed some active metals from the catalyst and was permanently adsorbed on the surface. Tetrahydrofuran was deemed the best

solvent because it can be removed easily from the catalyst and does not remove active components.

A yield-based reactor model for Gulf's P-99 SRC-II process was developed and inserted into the ASPEN simulator. Convergence of the entire process flow sheet, including recycle streams, was obtained. Further analyses are in progress.

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, a Wilsonville vacuum bottoms sample produced during run 242 was fractionated in the Fractional Distraction Unit (FDU) using solvents with different critical temperatures (T_C). The following solvents were used: n-pentane ($T_C = 196.8^\circ\text{C}$), cyclohexane ($T_C = 280.4^\circ\text{C}$), and toluene ($T_C = 320.8^\circ\text{C}$). The experiments were all run at a reduced temperature (T_R) of 1.01. The amount of vacuum bottoms brought overhead with these solvents was 18%, 49%, and 62%, respectively. This demonstrates that the depth of fractionation can be controlled by appropriate choice of solvent and that in the case of cyclohexane, a large fraction of the bottoms can be distracted at temperatures less than 300°C. Also, no distraction is observed at a reduced pressure (P_R) of 1.0 for any of the solvents; however, operating at a P_R of 2.0 resulted in initial overhead rates of greater than 12 grams of vacuum bottoms per gram-mole of solvent when either cyclohexane or toluene was used.

The hot-finger section of the distraction column was modified this quarter to permit better monitoring of the temperatures in this zone. The top of the column was reworked to incorporate a flanged fitting that allows the hot finger to be

removed for inspection and also permits attachment of thermocouples directly on the surface of the hot finger. Except in the initial phase of testing the unit with vacuum bottoms, the hot finger has not been energized. In the process variable studies discussed above, the destruction vessel was operated isothermally so that basic destruction data could be collected.

Plans for next quarter include continuing the investigation of the primary process variables in the FDU. The influence of pressure in the region from P_R of 1.0 to 2.0 will be studied, as well as the effect of using the hot finger to establish reflux in the column. These tests will culminate in a set of pseudocomponents that will be used in the characterization studies planned for the Wilsonville vacuum bottoms.

ASPEN Modeling

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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 provides 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 utilizing 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, key sections of the P-99 flowsheet were inserted into the ASPEN simulator, and the program for the entire process was converged. A yield-based reactor model was constructed and used as the reactor module. While yields of individual compounds are readily available in Gulf reports, the yields of pseudocomponents in the distillate range, not to mention those comprising SRC, are typically not found. The missing pseudocomponent yields for narrow distillate fractions were therefore estimated from boiling point profiles given for the major internal streams, and the yields of nondistillate fractions

were assumed to decrease linearly with increasing assigned boiling points. The assumption of such a linearly decreasing distribution for SRC fractions had empirically been found last quarter to give reasonable results in simulations of downstream separation vessels.

Nonconventional substreams and their attributes were defined in order to take advantage of ASPEN capabilities for handling solids. Conversion of coal to more "conventional" liquids and gases, and allowance for mineral matter and inert organics in downstream sections are now being simulated in a more natural fashion. Gas and liquid recycle streams were incorporated into the ASPEN simulation, and strategies were devised via splitter blocks for controlling the stream ratios and/or compositions. The presence of the recycle loops tested ASPEN's procedure for "tearing" streams, assigning initial estimates to input parameters, and proceeding to successful convergence via built-in algorithms.

As previously reported, the use of the Benedict-Webb-Rubin-Starling (BWRS) equation of state generally gave larger deviations from experimental results for flow rates in major separation vessels of the P-99 than the Redlich-Kwong-Soave-ASPEN equation of state. An improved version of the BWRS equation of state applicable to polar and associated fluids became available through a FY83 DOE grant to the University of Oklahoma, and its use in ASPEN is being investigated. Implementation is being attempted in cooperation with the Oklahoma researchers.

Next quarter a number of P-99 data sets, representing test runs at different operating conditions and changes in feed coal, will be simulated with ASPEN, and comparisons drawn between calculated and experimental flow rates and compositions. A kinetic reaction model for predicting process yields will be investigated for possible insertion as a reactor module.

Transport Studies in Coal Liquefaction

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Coal Conversion Engineering Branch*

The objective of this project is to conduct engineering research directed toward effectively transporting coal and understanding the phenomena governing fluid/solid transport as related to conventional and novel coal liquefaction techniques.

During this quarter, work was performed in the following areas:

A. Design and Operation of a Bench-Scale Preheater for Coal/Water Mixtures

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 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.

Relative to the amount of batchwise work reported to date concerning the chemistry of coal liquefaction in the presence of water, the amount of process engineering related study that would be required to do continuous processing is much less. Such a processing approach would employ 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 will operate in the supercritical region with respect to the water and reducing gas mixture. Vapor and liquid products will 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 a bench-scale preheater in which a coal/water slurry under high pressure is heated from subcritical to supercritical conditions, 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.

A literature review of fluid/solid transport with application to a process for water-assisted

coal liquefaction is currently being conducted in order to develop criteria for the design of such a bench-scale preheater. From this review, recommendations will be developed for designing a bench-scale preheater for the particular case of heating a slurry of -200 mesh coal and water ~ 4000 psig over a temperature range of ambient to 400°C with the possible presence of hydrogen, carbon monoxide, or synthesis gas as an auxiliary transport fluid.

B. Viscometer Development for Coal/Oil Slurries

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 previously tested on several Newtonian liquids with an error not exceeding 5%. For this study, a 2.5-L stirred autoclave serves as the pressure/reaction vessel. A schematic diagram of the viscometer apparatus is shown in Figure 2. Fluid is sampled (300 cm^3 maximum volume) by opening the inlet valve to couple the viscometer pump with the autoclave and withdrawing a 2-inch-diameter piston actuated by 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 (0.09-in.-i.d. x 13.7-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.

In the tests performed this quarter, the viscosity of a heat transfer fluid and a coal-derived liquid have been measured at ambient temperature and at pressures ranging from atmospheric to 2000 psig. Each series of viscosity measurements was performed under both nitrogen and helium atmosphere. Data from these experiments will investigate the effect of pressure and gas solubility on liquid viscosity.

The capillary tube viscometer used in the previous study is currently being modified for use in measuring the viscosity of coal/oil slurries at elevated temperature and pressure. As

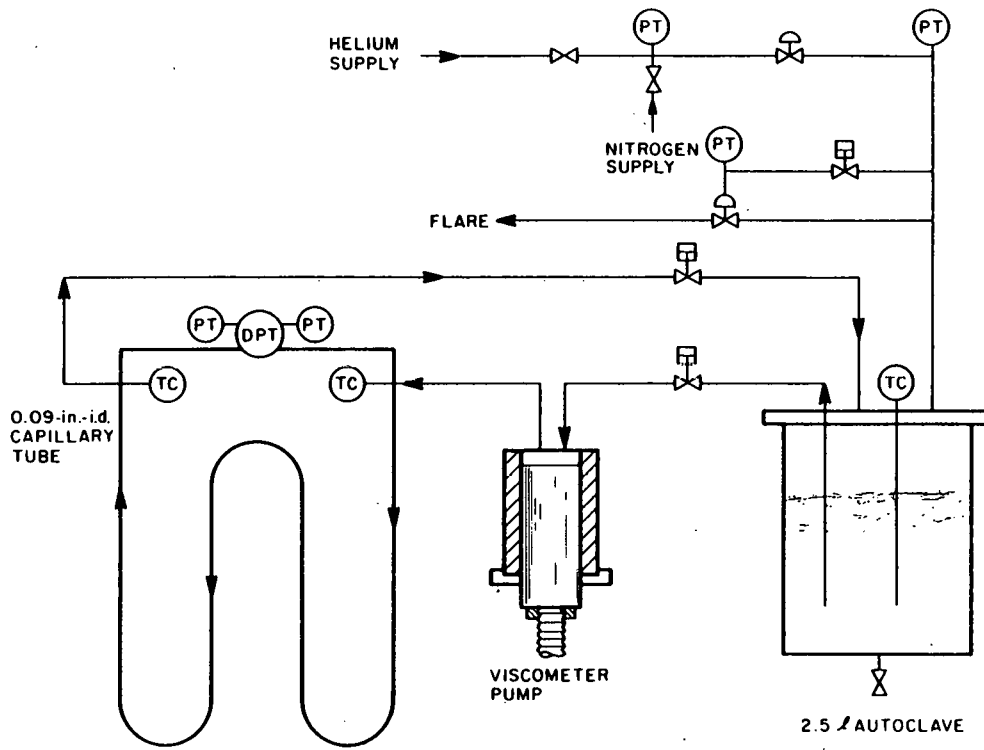


Figure 2-Original capillary tube viscometer.

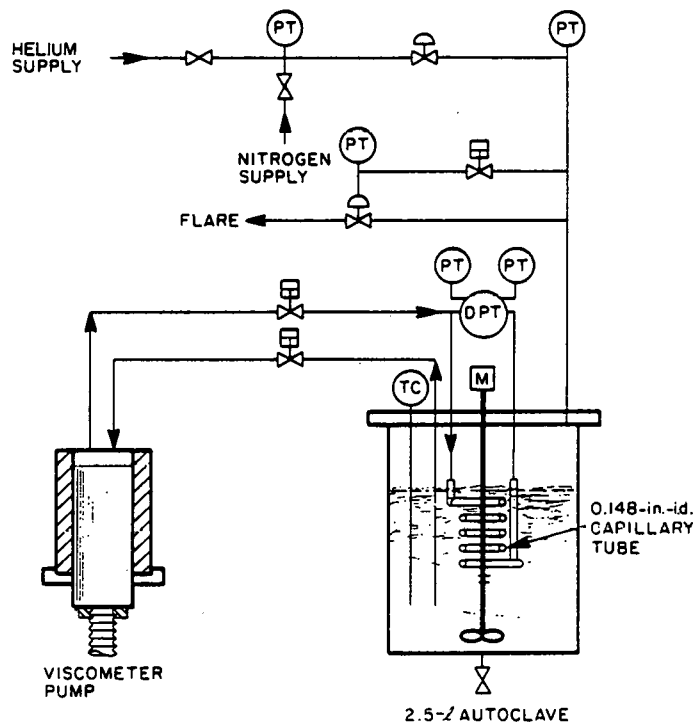


Figure 3-Improved capillary tube viscometer.

shown in Figure 3, a new capillary tube (0.152-in-i.d. x 18-ft-long) will be coiled and inserted in the autoclave. By having the capillary immersed in the test fluid at conditions of temperature and pressure, the need for a separate capillary tube heating circuit is eliminated. Once modifications are completed, testing will begin with reference fluids at ambient temperature and pressure. Subsequent testing will include viscosity measurements of the reference fluids and coal/oil slurries at conditions of elevated temperature and pressure.

Catalyst Preparation and Characterization

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B.D. Blaustein, Chief,
Process Sciences 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 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 project is very closely coordinated with the project on Fundamentals of Coal Conversion Catalysts being conducted by the Coal Conversion Engineering Branch.

A series of Ni-Mo/Al₂O₃ catalysts was prepared containing a constant loading of NiO + MoO₃ but with promoter ratio (defined as $R = \text{Ni}/(\text{Ni} + \text{Mo})$) varying from 0 to 1. These catalysts were characterized by chemical and BET analysis, and their activity was determined in a batch hydroprocessing unit. The results in Table 23 show that the activity of the catalyst for converting feed to cyclohexane-soluble material is a weak function of R up to a value of 0.5, above which its activity drops off rapidly. A similar trend is seen in hydrogenation and HDN activity. Only the HDS activity shows the significant promotional effect expected with increasing promoter ratio. The optimum promoter ratio for hydrogenation and HDN occurs at $R = 0.4$; however the effect is small. The amount of coke deposited on

the catalyst during the batch test appears to be independent of R, while the H/C ratio shows a weak maximum near $R = 0.5$.

Preparation of a series of Ni-W/Al₂O₃ catalysts is nearly complete. These catalysts will be used to determine the optimum R and loading level in the Ni-W/system. A large batch of 5Ni-20W/Al₂O₃ was prepared for use in the continuous hydroprocessing unit.

Twenty spent catalyst samples from Wilsonville's Run 243 are being characterized with respect to their physical and chemical properties. Table 24 gives preliminary data determined by BET techniques for tetrahydrofuran-extracted samples. Chemical analysis of the spent catalysts is in progress. Mercury porosimeter characterization of selected samples remains to be done. Due to lack of sufficient sample, activity measurements were performed only on one Run 243 sample (sample No. 12659, for which a one-gallon sample was obtained). Portions of this sample were extracted in cyclohexane, ethyl acetate, tetrahydrofuran, or pyridine prior to their activity determination. The results in Table 25 show that differences in activity are only slightly dependent on the nature of the solvent used for extraction. Chemical analysis of the extracted catalysts showed a slight loss of nickel in the pyridine-extracted sample, which is consistent with the nickel molybdate found in the ashed pyridine-soluble extract. Therefore, it appears that tetrahydrofuran is a better choice than pyridine as the extraction solvent, since it can be completely removed from the catalyst by vacuum-drying at 100°C and does not remove active components from the catalyst during the extraction. In addition to Run 243 samples, a series of spent catalysts from Run 244 was obtained during the last quarter.

The results of our studies on the activity and characterization of spent and regenerated (by carbon burn-off) catalyst samples from Wilsonville's Run 242 and Lummus' Run LCF-9 were presented at the Direct Liquefaction Contractors' Meeting held on November 16-17, 1983, in Pittsburgh.

Fundamental Studies in Coal Conversion Catalysis

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J.A. Ruether, Chief,
Coal Conversion Engineering Branch*

The objective of the proposed research is to provide fundamental data on the hydroprocessing

Table 23.
Results of Ni/Mo Effect on Upgrading

A: Fresh Catalyst Characterization											
Ni (wt%)	0	0.8	1.6	2.6	3.3	4.5	5.4	7.1	9.2	11.1	12.8
Mo (wt%)	13.6	11.5	10.4	11.3	8.6	7.9	7.1	5.7	4.5	1.9	0.0
Ni/Mo Ratio	0	0.10	0.20	0.27	0.39	0.48	0.55	0.67	0.77	0.91	1.00
SA (m ² /g)	177	181	182	184	179	185	191	188	190	181	164
PV (cc/g)	0.524	0.641	0.639	0.641	0.628	0.634	0.648	0.652	0.633	0.634	0.625
APD (Å)	119	142	140	139	140	137	136	139	133	141	152
B: Activity Data ^a											
Ethyl acetate-solubles conv. (%)	69.9	67.3	68.6	71.5	70.8	71.0	68.4	68.1	64.0	56.7	46.1
Cyclohexane-solubles conv. (%)	56.1	57.0	59.0	61.8	61.6	60.3	54.9	49.5	41.1	38.1	25.1
H/C Ratio	1.032	1.020	1.034	1.044	1.055	1.050	1.045	1.035	1.018	1.004	0.970
Δ H/C Ratio (%)	11.6	10.3	11.8	12.9	14.1	13.5	13.0	11.9	10.1	8.5	4.9
HDN (%)	22.9	28.7	24.4	26.7	30.5	25.2	24.4	19.9	16.8	11.5	7.6
HDS (%)	48.7	61.5	69.2	74.4	74.4	74.4	69.2	69.2	64.1	51.3	46.1
C. Spent Catalyst Characterization											
Coke (%) ^b	—	13.7	13.9	13.6	13.3	10.8	13.3	14.2	14.1	13.9	14.0
H/C Ratio	—	1.25	1.23	1.37	1.18	1.63	1.40	1.30	1.31	1.22	1.12

^aTest Conditions: 150 g SRC, 150 g Hydrogenated Creosote Oil, T = 415°C, P = 2000 psi, Hydrogen flow rate = 8 SCFH, and t = 60 min.

^bCoke defined as weight percent carbon + hydrogen.

Table 24.
Properties of THF-Extracted Catalyst Samples From Run 243

Catalyst Age (# SRC/# Cat)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Av. Pore Diameter (Å)	LOI ¹ (450°C) (wt%)
Series A				
0	167	0.360	100	6.4
8.5	147	—	—	15.6
36.5	149	—	—	18.6
63.0	143	0.263	90	17.3
210.0	148	—	—	15.2
254.0	156	0.2892	80	11.8
443.0	145	—	—	13.4
467.0	136	—	—	15.4
575.5	154	—	—	10.6
814.7	158	0.295	80	10.4
868.8	145	—	—	10.6
978.8	158	0.289	80	9.3
Series B				
0	163	0.328	100	11.5
7.0	164	—	—	12.7
56.0	162	0.289	80	13.5
116.0	148	0.243	80	15.3
137.0	157	0.295	80	13.4
179.0	154	—	—	15.4
273.1	140	0.247	80	13.5
328.0	144	0.254	80	14.4

¹LOI = weight loss that occurs when the sample is calcined at temperature to constant weight.

Table 25.
Batch Activity Data for Wilsonville Sample 243 (SN 12659) After Extraction

Sample	Base Line	Sample Extracted in			
		Cyclohexane	Ethyl Acetate	Tetrahydrofuran	Pyridine
Ethyl Acetate-Solubles Conversion (%)	57.7	46.5	49.1 ± 6.1	51.0 ± 1.8	52.9 ± 4.9
Cyclohexane-Solubles Conversion (%)	53.5	46.6	48.7 ± 10.8	48.7 ± 0.9	47.3 ± 0.9
H/C Ratio in Product	1.033	1.027	1.026	1.030 ± 0.001	1.034 ± 0.002
% Δ H/C	12.1	11.0	10.9 ± 0.6	11.3 ± 0.1	11.8 ± 0.1
% HDN	24.4	26.7	24.2 ± 4.1	29.0 ± 0.1	26.7 ± 3.2
% HDS	71.8	66.4	56.4 ± 9.2	62.8 ± 1.3	64.1 ± 0.1
% HDO (difference)	67.8	71.5	54.8 ± 15.7	53.8 ± 0.3	37.4 ± 5.6

Test Conditions: T = 415°C, P = 2000 psi, H₂ flow rate = 8 SCFH, t = 60 min.; 50 wt% SRC in Hydrogenated Creosote Oil.

Table 26.
Properties of Catalyst Used to Investigate the Effect of Pore Size Distribution

Catalyst	NCT-60880	RET-60970	RET-50931	RET-51480	RET-51042	RET-50950
Bulk Density (g/cm ³)	0.734	0.707	0.685	0.641	0.699	0.622
Pellet Density (g/cm ³)	1.47	1.40	1.30	1.22	1.27	1.29
Pore Volume (cm ³ /g)	0.420	0.443	0.492	0.554	0.509	0.511
Surface Area (m ² /g)	250	244	246	152	106	87
Average Mesopore Diameter (Å)	84	86	120	165	206	270
NiO (wt%)	3.44	3.57	3.44	3.50	3.31	3.44
MoO ₃ (wt%)	18.53	18.53	18.15	15.80	18.00	15.83
Al ₂ O ₃ (wt%)	70.39	70.95	69.53	75.96	71.14	76.62
Na ₂ O (wt%)	0.13	0.13	0.13	0.13	0.26	0.13
Metals Loading (g/cm ³ of catalyst)	0.161	0.156	0.148	0.122	0.149	0.120

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 and will provide direction for further investigations leading to process improvements.

The investigation of the effect of catalyst pore size distribution on the conversion of short-contact-time SRC was completed. The properties of the catalysts used in this study as well as in the one using an SRC-II/creosote oil feedstock are presented in Table 26. As shown, as the pore size of the catalyst is increased, the surface area declines. The active metals were impregnated using identical procedures; therefore, the observed differences in metals loading between the catalysts are probably due to experimental error in the determinations of the concentrations of active metals and the bulk density. Regardless of the differences, all loadings are above those found previously for maximum activity. The activity data for those experiments employing SRC-I are presented in Table 27. Although no major differences were observed, it can be seen from the data in Table 27a that smaller pore catalysts appeared to have slightly higher hydrogenation and denitrogenation activities than the larger pore catalysts. No effect of pore size on desulfurization activity is apparent from the data in Table 27b; however, conversions of the cyclohexane-insolubles and ethyl acetate-insolubles (data not presented) were higher for those catalysts having average pore sizes in the midrange. These data appear to indicate that while the large pore, lower surface area catalysts have lower hydrogenation activity, they are allowing the larger molecules to enter the catalyst and react on the interior surface. For the smaller pore catalyst, only the smaller molecules that are mostly contained in the creosote oil solvent enter and react. The use of actual process-derived solvent may yield different results; therefore, such material will be used in future investigations.

Data from the analysis of the spent catalyst from the pore size investigation using SRC-I are presented in Table 28. As shown, the concentra-

tion of trace metals on the catalyst surface increases as the average pore diameter is increased. The H/C ratio of the catalyst also decreases with an increase in pore diameter. These two results are consistent with data reported previously at PETC [Stiegel, G.J., Tischer, R.E., and Polinski, L.M., I&EC Prod. Res. Dev., 22(3), 411 (1983)]. The concentration of sulfur on the spent catalyst also decreases with increasing pore diameter. However, although some data for molybdenum are suspect, the sulfur-to-molybdenum ratio is approximately two in all cases, the value expected for complete sulfiding.

Investigations of the hydroprocessing of low sulfur petroleum feedstocks and model compounds have indicated that the addition of hydrogen sulfide to the reactor can have beneficial effects on the desired reactions. Hydrogen sulfide has been shown to act as a hydrogen transfer medium and as a hydrocracking catalyst in hydrocarbon pyrolysis and model compound studies for coal liquefaction. Hydrogen sulfide added to the reactor will also increase the concentration of hydrogen sulfide present in the liquid phase. It is possible that under such conditions, the reaction equilibrium for the molybdenum-sulfiding reaction could be shifted to the right, thus maintaining the catalyst in a more highly sulfided, more active state. Preliminary runs were made during the third quarter of FY83 in the continuous flow unit at 780°F and 2000 psig using a 50 wt% mixture of SRC-I in creosote oil. Shell 324, presulfided using the standardized procedure reported previously, was used. The feed gas was a 1 mol% mixture of hydrogen sulfide in hydrogen. A comparison of the data from runs with and without hydrogen sulfide addition is presented in Figure 4. Data for the run without hydrogen sulfide addition were quite reproducible with two runs reported previously. As shown by the data, the addition of hydrogen sulfide had no effect on the conversion of cyclohexane-insolubles and ethyl acetate-insolubles (data not shown) and on hydrogenation activity. Except near the end of the run, denitrogenation and desulfurization activity was higher for the run with hydrogen sulfide addition. Conversions without hydrogen sulfide addition and without a catalyst were the following: Δ H/C = -2.75%; HDN = 9.8%; and cyclohexane-insoluble conversion = 16.6%. The enhancement in denitrogenation was expected based on model compound studies; however, hydrogen sulfide was expected to either inhibit or have no effect on desulfurization. The data show no sulfur could have been incorporated into the products. As shown in Table 29, the sulfur

Table 27a.
Activity Data for Catalysts Used in Pore Size Study

Catalyst I.D.	50880	50870	50931	51460	51042	50950
Average Pore Diameter (Å)	84	86	120	165	206	270
Surface Area, m ² /g	250	244	240	152	105	87
Time (hr)	Δ H/C, wt%					
10	14.5	13.4	13.0	14.5	9.7	10.2
22	13.5*	12.0	11.6	9.5	11.1	7.7
35	13.5	10.8	9.1	10.6	8.1	8.9
46	12.0	9.0	10.7	10.4	8.2	9.2
56	11.1	9.8	10.5	9.2	8.2	9.5
65	12.1**	10.7	8.5	9.3**	8.7	7.8
77	11.1	10.9	11.2	10.3	7.6	7.8
90	9.5	10.7	9.1	8.8	8.3	7.1
98	11.1	8.6	10.2	10.1	8.1	8.4
Time (hr)	Denitrogenation, wt%					
10	40.9	37.6	37.2	32.2	26.9	22.6
22	35.6*	29.6	31.8	30.4	24.0	22.6
35	34.7	31.4	29.2	29.5	30.1	22.6
46	34.7	25.2	41.7	30.4	25.7	22.6
56	32.9	24.3	25.6	26.0	29.2	22.6
65	32.9**	27.0	25.6	29.5**	27.0	22.6
77	32.9	27.0	26.5	29.5	28.7	20.9
90	32.0	19.8	27.4	28.6	24.4	22.6
98	31.1	25.2	25.6	15.4	25.2	22.6

*Sample collected at time = 24 hr

**Sample collected at time = 66 hr

Table 27b.
Activity Data for Catalysts Used in Pore Size Study

Catalyst I.D.	50880	50870	50931	51480	51042	50950
Average Pore Diameter (Å)	84	86	120	165	206	270
Surface Area, m ² /g	250	244	240	152	105	87
Time (hr)	Conversion of Cyclohexane-Insolubles, wt%					
10	61.9	65.5	70.1	72.2	66.5	62.7
22	56.9*	56.8	63.6	68.0	58.7	63.6
35	55.4	55.3	63.1	66.8	65.5	59.5
46	54.9	54.6	59.5	68.5	67.5	61.0
56	55.4	55.8	56.1	68.0	66.3	58.8
65	54.0**	52.6	72.5	61.1**	63.4	61.9
77	52.3	52.4	60.7	64.5	63.6	58.5
90	54.9	47.9	58.5	67.3	64.8	62.2
98	55.6	48.1	62.9	60.3	63.3	57.5
Time (hr)	Desulfurization, wt%					
10	73.6	70.5	76.2	72.1	69.2	78.3
22	71.4*	65.9	69.7	74.4	71.8	78.3
35	67.0	63.6	63.2	72.1	72.1	78.3
46	69.2	61.4	69.7	72.1	72.1	78.3
56	67.0	70.5	63.2	72.1	72.1	56.5
65	69.2**	61.4	67.6	76.7**	68.2	78.3
77	64.8	61.4	65.4	72.1	68.2	67.4
90	69.2	54.6	65.4	79.1	68.9	56.5
98	67.0	59.1	65.4	—	71.1	56.5

*Sample collected at time = 24 hr

**Sample collected at time = 66 hr

Table 28.
Composition of Spent Catalysts from Pore Size Study

Catalyst I.D.	50880	50870	50931	51460	51042	50950
Average Pore Diameter (Å)	84	86	120	165	206	270
Surface Area, m ² /g	250	244	240	152	105	87
Carbon, wt%	12.5	11.0	13.6		16.0	10.5
Hydrogen, wt%	1.5	1.3	1.4		1.4	0.9
Nitrogen, wt%		0.4	0.5			
Sulfur, wt%	6.7	6.7	6.5	6.1	6.3	6.2
H/C*	1.43	1.41	1.23		1.04	1.02
Titanium, wt%	0.5	0.2	0.8	0.8	1.1	1.2
Iron, wt%	0.2	0.6	0.3	0.3	0.4	0.6
Calcium, wt%	0.1	<0.1	<0.1	<0.1	0.2	0.2
Nickel, wt%	2.1	2.1	1.9	2.4	1.8	1.9
Molybdenum, wt%	10.5	9.8	6.5	7.6	9.1	9.1
(Ti + Fe + Ca)/Mo*	0.151	0.146	0.325	0.279	0.370	0.430
S/Mo*	1.91	2.05	2.99	2.40	2.07	2.04

*Atomic ratio

content of the spent catalyst from the hydrogen sulfide addition run was about 0.7 wt% higher than for the catalyst from the base-line run. The carbon concentration was also about 2 wt% higher. A run without the use of a catalyst but with hydrogen sulfide addition has been made to see if any of the observed results are due solely to hydrogen sulfide. A similar set of runs will be made using SRC and process-derived solvent from Wilsonville in order to confirm these results with a realistic feedstock.

Supported-metal hydroprocessing catalysts must be sulfided prior to use in order to convert the metals from their oxidic to their active sulfidic forms. The techniques by which this conversion is affected determine the extent to which the metals are converted. Sulfiding temperature is important in the initial conversion to the sulfidic state; however, as discussed above, reaction equilibrium may result in a shift to an unsulfided or par-

tially sulfided state when using a low sulfur feedstock. Three very preliminary tests were conducted to determine the effect of reaction temperature and start-up procedure on the sulfur content of presulfided Shell 324m. Shell 324m is slightly different than Shell 324 in that it has a slightly larger mesopore diameter (115 vs. 98Å) and a slightly lower pellet density (1.38 vs. 1.51 g/cm³). In the first test, the catalyst was heated up under flowing hydrogen to 355°C, at which time the flow was transferred to a 10 mol% H₂S/H₂ mixture. The temperature was lined out at 350°C and held for five hours. In the second and third tests, the catalyst was heated under flowing H₂S/H₂ and reacted for five hours at either 350°C or 400°C. Upon completion the unit was purged with nitrogen and then cooled, and the catalyst was collected and sent for analysis. The results showed that the sulfur content of the catalyst was increased from 5.7 wt% in test 1 to 6.7 wt% for test 2 to 7.1 wt% for test 3. Since these catalysts were subjected

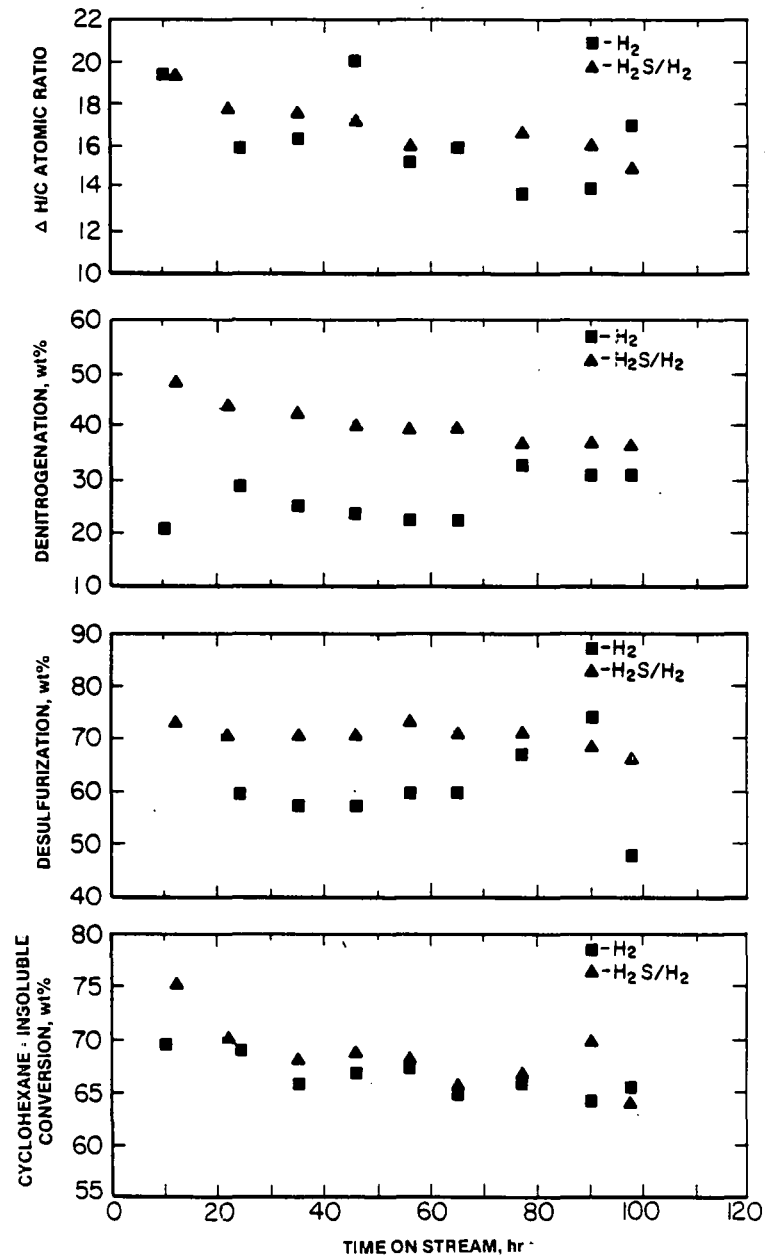


Figure 4- Effect of H_2S addition on the activity of presulfided Shell 324

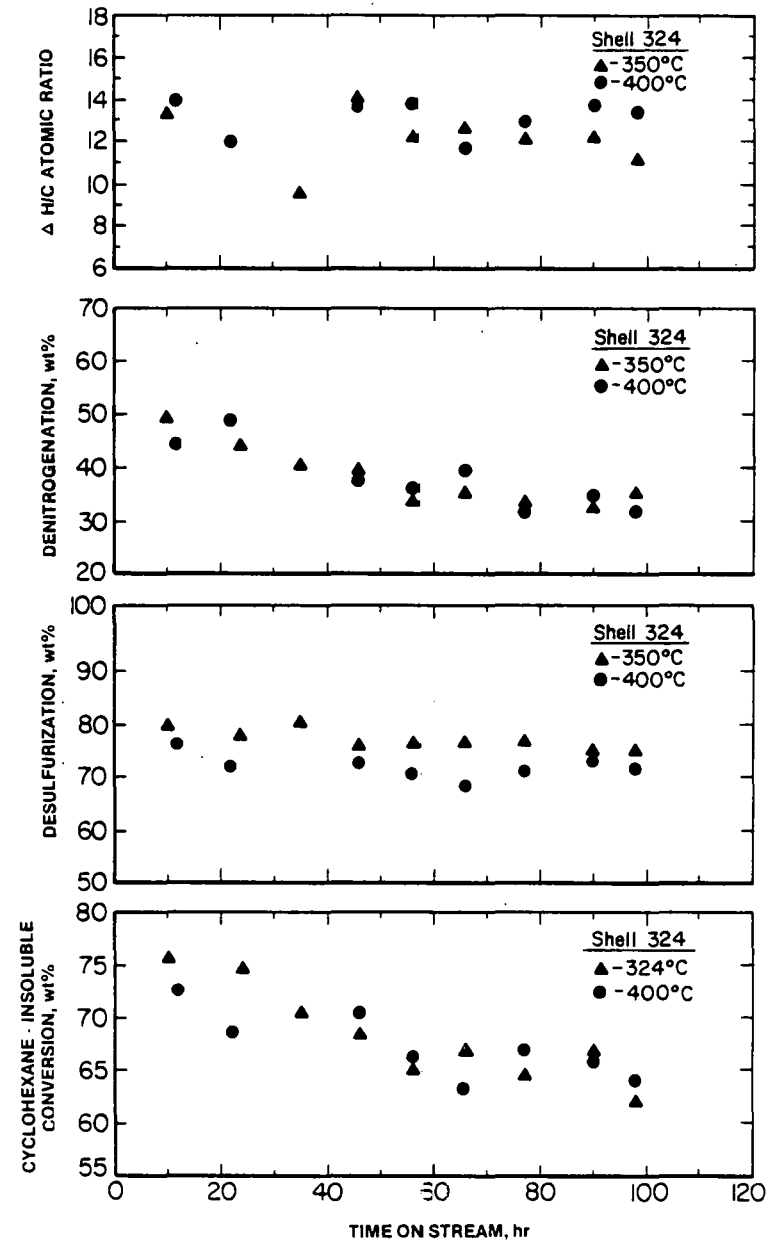


Figure 5- Effect of catalyst sulfiding temperature on the conversion of Solvent-Refined Coal

Table 29.
Analysis of Spent Catalyst Samples

	Shell 324		Shell 324m	
	no H ₂ S addition	H ₂ S addition	presulfided at 350°C	presulfided at 400°C
Carbon, wt%	13.2	15.1	12.8	11.4
Hydrogen, wt%	—	1.32	0.99	0.82
Nitrogen, wt%	0.6	0.6	0.5	0.5
Sulfur, wt%	6.3	7.0	6.8	6.6
H/C atomic ratio	—	1.04	0.92	0.86
Titanium, wt%	0.5	0.4	0.4	0.3
Iron, wt%	0.3	0.1	0.3	0.3
Calcium, wt%	—	<0.1	0.1	0.1
Nickel, wt%	—	2.2	1.8	2.1
Molybdenum, wt%	—	9.0	9.0	8.1

to conditions not normally used in a run, the results may not be truly representative of the sulfur content of the catalyst in the reactor at the start of a run.

To determine the effect of start-up conditions and reaction temperature on the activity of the catalyst, presulfiding procedures used for tests 1 and 3 were employed. After sulfiding was terminated, the unit was pressurized with hydrogen to 2000 psig and heated to 416°C. At about 400°C, the feedstock containing 50 wt% SRC-I in creosote oil was introduced. The results of these two runs are presented in Figure 5. As shown, there was essentially no difference in catalyst activity regardless of the start-up and presulfiding procedure, even though initial tests indicated that procedure 3 should have resulted in more effective sulfiding. It is interesting to note that the sulfur contents of the spent catalyst from these two runs, as shown in Table 29, are almost the same. In fact, almost no differences exist between the two samples. A comparison of the activity data for these runs with those obtained with hydrogen sulfide addition shows no differences in activity. Unfortunately, because of differences in the catalyst as well as the composition of the creosote oil (especially the hydrogen content), direct comparisons of the data are not justified.

Almost all bench-scale investigations concerned with the hydroprocessing of Solvent-Refined Coal employed creosote oil as the solvent rather than process-derived material. Process-derived solvent and SRC were obtained from Wilsonville and processed thermally in a continuous flow reactor at 720°F and 750°F and 2000 psig with a residence time comparable to that experienced during catalytic runs. No denitrogenation, desulfurization, and cyclohexane-insoluble conversions were observed at either reaction temperature. No hydrogenation/dehydrogenation activity was present at 720°F; however, dehydrogenation of the feedstock occurred at 780°F. Approximately 10-wt% conversion of the preasphaltene fraction was observed. Because of the low thermal conversions, this feedstock is an excellent choice for use in catalytic studies.

Until recently, the hydroprocessing step of two-stage coal liquefaction was concerned primarily with heteroatom removal; however, attention is now being focused on hydrogenation activity instead. Because Ni-W/Al₂O₃ catalysts are superior to Ni-Mo/Al₂O₃ catalysts for aromatic hydrogenation, preliminary tests have been conducted to determine the activity of, and to obtain experience with, Ni-W/Al₂O₃ catalysts. A PETC-prepared Ni-W/Al₂O₃ catalyst having a composition similar to that of a commercially prepared

catalyst was processed in the continuous flow unit at both 720°F and 750°F and 2000 psig with a 50-wt% mixture of SRC in process-derived solvent. Preliminary results indicate that the conversions at 720°F and 750°F, respectively, are the following: $\Delta H/C = 1.3\%$ and 13% to 14% ; HDN = 25% and 30 to 40% ; HDS = 85% and 89% ; ethyl acetate-insoluble conversion = 85% and 85% ; and cyclohexane-insoluble conversion = 74% and 81% . Based on these results and those from batch reactor tests, a reaction temperature of 735°F and a space velocity of $0.6\text{ cm}^3\text{ SRC/hr/cm}^3\text{ catalyst}$ were chosen as standard conditions for future catalytic runs. A base-

line run using Shell 324 will be performed for comparison purposes.

Preparation of the process area for the new continuous-flow hydrotreating reactors is proceeding well. All of the old process equipment and asbestos insulation have been removed from the required areas. Layout and construction drawings for the new units and supporting facilities are being prepared. Specifications for the testing and relocation of the vessel to be used for high pressure hydrogen storage have been prepared. Renovation of the floor and painting of the area should begin shortly. Construction of the units will begin thereafter.

INDIRECT LIQUEFACTION

R.R. Schehl, Coordinator

This program is directed toward developing a better fundamental understanding of catalyst properties, reaction mechanisms, and reactor hydrodynamic 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/structural features of catalysts that relate to catalyst formation and use; the application of appropriate methodology for the analysis of indirect liquefaction products; and finally, the investigation of hydrodynamic phenomena in nonreacting model systems to provide sound basis for the design of slurry bubble column reactors.

This quarter, studies were conducted to determine the effect of calcination temperature on pore size distribution of precipitated iron catalysts for liquid-phase Fischer-Tropsch synthesis. The pore size of a catalyst calcined at 400°C was nearly five times larger than that of an uncalcined catalyst. Procedures have been developed to determine structural and chemical properties of Fischer-Tropsch catalysts sampled from a slurry-phase reactor during operation. Preliminary studies indicate that XPS and ISS analysis of the catalyst surface is possible after proper preparation of the wax-encapsulated catalyst. Gas chromatographic methods for the analysis of

Fischer-Tropsch liquid and wax samples for functional groups across a carbon number range of C_8 to C_{40} have been established and should be available for routine use in the next quarter. Further hydrodynamic tests were conducted in a 10-cm bubble column with water-ethanol mixtures to investigate slurry frothing phenomena. Results were in qualitative agreement with a dynamic surface tension model of the gas-liquid system.

Synthesis Gas Chemistry

V. Udaya S. Rao, Cost Account Manager
Bernard 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 (a) metal crystallite size (i.e., degree of dispersion), (b) the pore size distribution of the catalyst and the support, (c) metal-support interactions, (d) presence of promoters in the catalyst, and (e) 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 a minimum of carbon formation on the catalyst and a low methane yield. Typical catalysts, such as precipitated iron and Fe-Mn, will be 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 active 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.

With the objective of determining the role, if any, of the pore size distribution on the conversion and product selectivity of Iron Fischer-Tropsch catalysts, an iron catalyst was prepared using the precipitation technique. After drying the precipitate in air at 100°C, the catalyst was calcined at 250°C, 300°C, 350°C, and 400°C for 20 hours. Calcination resulted in significant changes in the surface properties of these catalysts (see Table 30).

While the surface properties varied in the predicted fashion, of probably greater significance is the fact that the surface properties of other carbided catalysts measured previously differ little from those for the present catalyst calcined at 400°C. It will not be known conclusively if there is any significant difference in the surface properties of the carbided, calcined catalysts. Microreactor studies currently in progress indicate that after two weeks on stream, there is little difference in the performance of the uncalcined catalyst and the catalyst calcined at 400°C.

As a prelude to examining reaction pathways for CO + H₂ conversion over FT-ZSM-5 in single-stage and two-stage conversion, the primary FT products from silica-supported cobalt are being studied. The intention is to investigate the dependence of product selectivity on cobalt crystallite size. Two Co/SiO₂ catalysts were prepared and tested for 1H₂/1CO syngas conversion at 280°C. One was a 6% Co/SiO₂ prepared by impregnation with aqueous cobalt nitrate solution, and the other a 2% Co/SiO₂ prepared by impregnation with dicobalt octacarbonyl. They showed comparable CO conversion (60% to 70%), low selectivity to methane (10%), and high selectivity to C₅+ (70% to 80%). The product from the nitrate preparation showed a higher 1-olefin/n-paraffin ratio in the C₅-C₁₀ range than that from the car-

bonyl preparation. Chemisorption studies on, and magnetic measurements of, these catalysts are being performed to determine the cobalt crystallite size.

Small particle H-ZSM-5 (0.1 μ) has been prepared and tested for ethylene conversion at 320°C. The sample showed a lower deactivation rate compared to the 1-μ-particle-size H-ZSM-5 sample used earlier. The 0.1-μ-particle-size H-ZSM-5 sample prepared at PETC showed steady C₂H₄ conversion and selectivity to aromatics over a 48-hour period and in these respects was comparable to a Mobil sample of H-ZSM-5 tested under the same conditions (See Figure 6). The small particle H-ZSM-5 will be used in the study of reaction pathways for syngas conversion over Fischer-Tropsch ZSM-5 in the combination processes (single-stage and two-stage).

Preparation of a large master batch (2100 gms) of 20Fe/80Mn catalyst for slurry-phase studies was completed. Catalysts from sixteen precipitations were combined to obtain this master batch. The resulting batch was ground to -100 mesh, homogenized, and stored under nitrogen. All subsequent samples for activity and characterization studies will be taken from this master batch. Samples from the master batch and eight of the individual preparations were submitted for chemical analysis. Twenty-gram portions of the master batch were calcined in air or nitrogen at 275°C for four hours. Samples of these calcined samples and the master batch were submitted for characterization using XRD, BET, and SEM techniques.

Construction of a temperature-programmed desorption apparatus (TPD) to probe the chemisorptive properties of the activated Fe-Mn catalysts is underway. The mass spectrometer has arrived and has been installed. A MINK microprocessor was interfaced and control software loaded. It will also be used for data acquisition. The temperature programmer has arrived and is being packaged into a control unit. The design for the desorption furnace will be put in final form upon completion of a review of the literature on TPD.

In the area of slurry-phase reactor studies, a slurry sampling device was installed on the slurry reactor feed line. By closing and opening respective valves, a sample of the slurry can be withdrawn into a helium-purged vial. The catalyst in the slurry is then concentrated by settling in the liquid wax that is heated in a furnace. The vial is then broken and the wax-encapsulated catalyst is studied using various analytical surface techni-

Table 30.
Effect of Calcination on Pore Size
Distribution of Precipitated Iron Fischer-Tropsch Catalysts

Calcination Temperature, °C	Surface Area m ² /g	Pore Volume cc/g	Pore Size Distribution, Å
—	153	0.20	37.5
250	127	.21	47.5
300	80	.19	72.5
350	50	.17	115
400	40	.16	170

Pore size distribution refers to the pore diameter where the pore volume is a maximum.

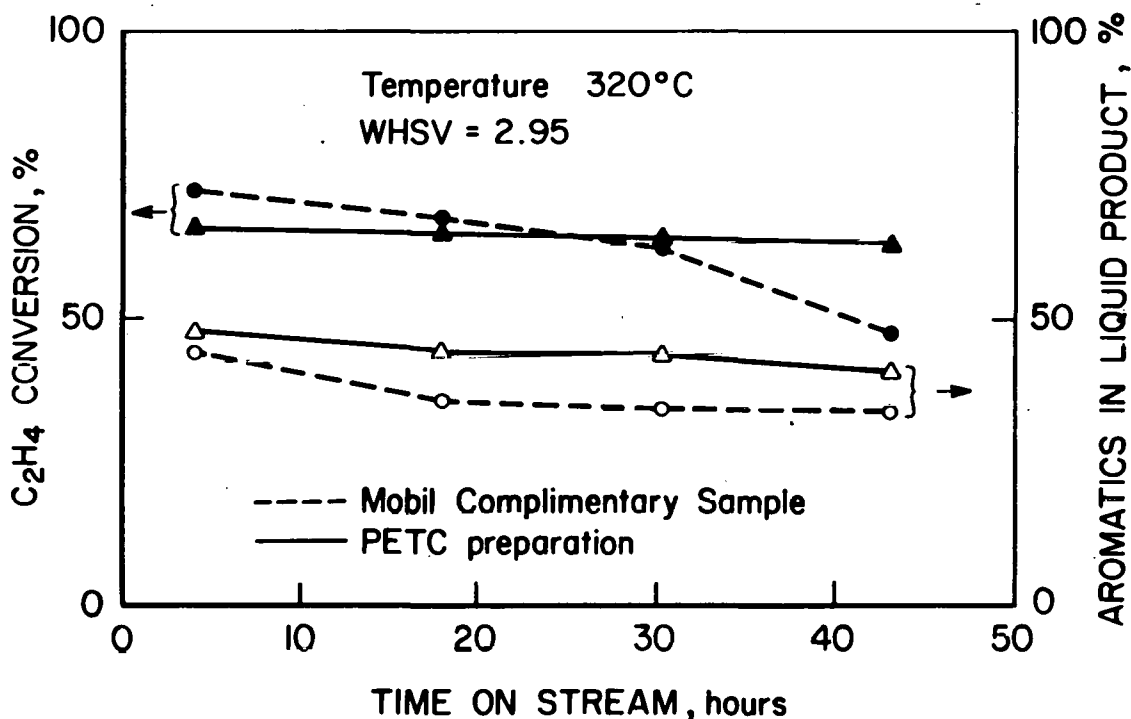


Figure 6-Ethylene conversion over small particle (0.1 μ) H-ZSM-5

ques. A test with fused iron at 260°C, 300 psig, and a space velocity of 250 hr⁻¹ of 1H₂/1CO synthesis gas was conducted to test the operability of the sampling device. Samples were successfully taken after 0, 43, and 200 hours on stream. Analytical results of these samples will be correlated with the activity and selectivity of the catalyst.

Using a Berty reactor, two catalysts, cobalt-thoria-ZSM-5 without an alumina binder and cobalt-thoria alumina with an alumina binder, were investigated with 1H₂/1CO synthesis gas at 280°C and 300 psig for 200 hours. At the end of the individual tests, an attempt was made to regenerate the catalyst. Carbonaceous material depositing on the catalyst during operation was oxidatively removed from the catalyst by burning in 1% oxygen in nitrogen at 350°C and then in air at 350°C and 400°C. With either catalyst after successive regenerations, the activities were always lower than the initial activity. However, product selectivities before and after the regeneration of a particular catalyst were similar, as determined by carbon number distribution and functionality of the liquid oil produced. This is in contrast to results with a cobalt-thoria-ZSM-5 catalyst with an alumina binder, where product functionality changed after identical oxidative regenerations. Catalyst samples that were withdrawn before and after regenerations are being studied via X-ray diffraction techniques in an effort to examine possible correlation of the phases present with the catalyst activity, product selectivity, and stability.

In the next quarter, the role of pore-size distribution will be investigated further. A catalyst prepared by burn-off of a cellulose-like material incorporated into the catalyst during the precipitation step will be studied. In addition, initial TGA and microreactor results will be reported for catalysts prepared by impregnation of controlled-pore-size supports with iron carbonyl compounds. Chemisorption and magnetization studies of Co/SiO₂ catalysts will be conducted to determine cobalt crystallite size. Experimentation will begin in the slurry reactor with an iron-manganese catalyst that has been activated by various techni-

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 concerted effort to describe those features of catalysts that relate to the production of liquids during catalytic coal liquefaction.

This quarter, the X-ray diffraction investigation of changes in the unit cell dimensions of the zeolite ZSM-5 as a function of the adsorption of hydrocarbons was continued. The adsorption of aromatic hydrocarbons decreased the unit cell dimension along the a axis and increased the b axis dimension. An opposite change was observed when paraffins were adsorbed into the channels of ZSM-5. Such behavior may be associated with the retention of aromatic hydrocarbons at locations in the channels of ZSM-5 that are different than the locations at which the paraffins are retained.

An XPS and ISS study of Fe and Fe/Mn catalysts that are immersed in reactor wax has begun. These initial studies have shown that XPS or ISS analysis during He⁺ or Ar⁺ depth-profiling of the as-received, catalyst-in-wax samples may not provide data, within a convenient time period, on the concentrations and oxidation states of the metals. As a result, a toluene or carbon disulfide washing of the catalyst-in-wax samples has been employed to remove some of the wax on the surface of the catalyst particles before XPS or ISS analysis. This washing has permitted the observation of surface concentrations of Fe, K, and O in a fused-Fe catalyst and has shown that the surface concentration of K is much higher than its bulk concentration. Next quarter, CS₂- or toluene-washed Fe/Mn catalysts will be investigated with XPS to determine dispersion and oxidation states of the metal components.

Product Characterization

*G.A. Gibbon, Cost Account Manager
H.L. Retcofsky, Chief,
Analytical Chemistry Branch*

The objective of this project 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 F-T process.

The use of multitechnique analysis during FY83 identified the best techniques to be used for cer-

tain 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, a gas chromatograph has been set up for the analysis of wax products for iron-catalyzed F-T reactions. A second chromatograph, for the liquid products from the same reaction, will be ready for use in the next quarter. Both chromatographic analyses are applied after the sample has been characterized for functional groups by infrared spectroscopy. When both chromatographs are fully operational, the analysis of the liquid and wax samples for functional groups across a carbon number range of C₆ to C₄₀, should be a well-routinized procedure.

Preliminary design work has begun on a two gas chromatograph system for the analysis of gaseous and liquid samples from a pair of reactors in series. The first reactor will be an iron-catalyzed F-T reactor; the second will be zeolite-catalyzed. The ability to analyze products from both reactors (and hence the feed to the second reactor) will allow a better understanding of the reactions occurring in both reactors.

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 properties play a large role in determining 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 phase holdup, bubble size and velocity distributions, and absorption coefficients, will be measured in organic liquids having similar bulk transport properties to F-T reactor

fluids. The measurements will be compared, to the extent possible, to transport properties obtained in an F-T reactor.

In addition, a review of major technical problem areas in the design of slurry bubble column reactors for F-T synthesis will be performed. This review will be helpful for identifying important parameters that influence catalytic reaction rates and serve as a basis for design simulation of F-T reactor performance over a desired range of operating conditions.

During this quarter, a series of tests has been completed with various liquids to obtain gas holdup in a 10-cm-i.d. bubble column. Various concentrations of ethanol in water were selected to determine the flow regime and frothing characteristics of the liquid. The maximum frothing ability, associated with a maximum gas holdup, occurred with a dilute concentration of ethanol (1.9 wt%). Either an increase or decrease in ethanol concentration reduced the frothing ability of this two-component system. This result is in qualitative agreement with a dynamic surface tension model of the gas/liquid system. A report on these results and associated bubble dynamics measurements has been presented at the PETC Indirect Liquefaction Conference held in Pittsburgh on October 12-13, 1983.

A flow regime map has been developed for perforated and sintered plate distributors based on gas holdup as a function of superficial gas velocity. Three distinct flow regimes have been encountered in 10-cm-i.d. and 10.8-cm-i.d. bubble columns: bubble, churn or churn-slug, and frothing. For all systems tested, bubble flow was observed up to superficial velocities of about 6 cm/s. For higher gas velocities, either frothing or churn/slug flow was observed, depending on the liquid composition.

A series of tests was performed in a nitrogen/water/glass bead system to determine the effect of solids concentration on gas holdup. Four different solids concentrations (9.1, 16.7, 23.1, and 28.6 wt%) were employed in the slurry. The gas holdup for the slurry system was always lower than the gas holdup for pure water. A marked decrease in gas holdup was observed for the three highest solids concentrations. For the water and water/9.1 wt% solids systems, slugging flow was observed, but for the other slurry systems, slugging flow did not occur.

The effect of liquid superficial velocity on the frothing ability of a 0.5-wt% aqueous ethanol system was measured in a 10.8-cm-i.d. column equip-

ped with a perforated-plate distributor. The superficial liquid velocity was either 0 or 0.77 cm/s, and the superficial gas velocity was varied between 0.8 and 21 cm/s. For gas velocities below 5 cm/s, increasing liquid flow had no effect on gas holdup. However, at gas velocities between 10 and 21 cm/s, increasing liquid flow rate decreased considerably the gas holdup (53% to 83% holdup for no liquid flow and 17% to 23% for a liquid velocity of 0.77 cm/s). This dramatic decrease in gas holdup with liquid flow is possibly created by nonequilibrium conditions of the dynamic surface tension for frothing systems. This relatively small change in the operation of a bubble column sug-

gests a method to control gas holdup for frothing systems.

For the next quarter, construction of a hot, pressurized test unit for measuring bubble size, velocity, and holdup will be started. A series of tests will be performed for bubble characteristics in aqueous alcohol and binary alcohol systems. A relationship between liquid physical properties and operating conditions will be developed for the bubble characteristic measurements. Gas absorption rate measurements will be initiated for organic liquid systems. A review of the problem areas in the design of Fischer-Tropsch reactors will be completed.

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.

The results of several experiments designed to determine the voidage distribution in a liquid/solid fluidized bed indicate that for a system of monodensity particles of varying size, the variance of the local void fraction distribution increases with increasing liquid flow rate, while the variance of the distribution approaches zero as the voidage approaches one. These results are consistent with those reported by other researchers using monosized particles of varying density.

The effectiveness of a simple wastewater treatment system employing steam stripping as the sole treatment operation is being evaluated in reducing the contaminant concentration of Westinghouse gasification process wastewater to levels acceptable for reuse or discharge. Contaminant removal will be optimized by varying the stripping steam-to-wastewater ratio and the bottoms pH.

Evaluation tests of Southwest Research Institute's (SWRI) ESR/NMR mass flowmeter at high pressures in the High Pressure/Coal Flow Test Loop were completed. The performance of the flowmeter was evaluated using two different coals. All data obtained from the various instruments were transmitted to SWRI.

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 United States.

During this quarter, experiments utilizing the recently developed static probe continued. These experiments involve measuring the static potential generated by a solid being fluidized with nitrogen gas in a Plexiglas model to study flow-regime transitions and bubble characteristics. Due to extensive problems with the data acquisition system, especially the PDP 11/40 computer, the experiments were not completed. A backup data acquisition system utilizing a strip chart recorder has been installed so the experiments can be completed. Analysis of the data, however, will be more difficult and time-consuming. Figure 7 shows several examples of data obtained in

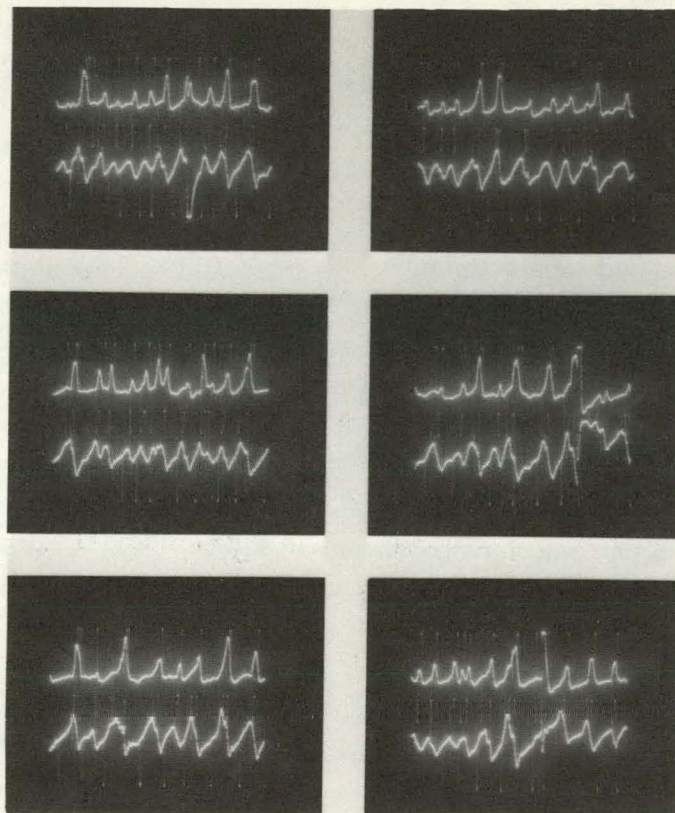


Figure 7

these experiments as they appear on the oscilloscope. Each waveform pair represents 10 seconds of real-time unit operation. Therefore, the data shown are only a small portion of the total data obtained in these experiments. Information obtained from the statistical treatment of these data will include average bubble diameters, bubble velocities, and gas holdups. In addition, bubble diameter and bubble velocity distributions will be determined.

Information obtained from previously conducted photographic experiments was presented at the AIChE Diamond Jubilee Meeting in Washington, D.C. A description of high-pressure fluidization and a film illustrating the conclusions drawn from this work were presented. A paper detailing the information contained in this presentation has been prepared for publication.

Preparations were begun for a series of experiments investigating bed expansion. The equipment has been inspected and necessary modifications have been made. Information concerning the effect of pressure on bed expansion is imperative for understanding the complex voidage-velocity relationships that exist in high-pressure fluidized beds. This complexity was made apparent by the observation of bed com-

pression in previously conducted fluidization velocity experiments. Parameters to be varied in these experiments are shown in Table 31. High-speed photographs will be taken to determine bed height and flow regime at the various conditions. When possible, the bed pressure drop will also be recorded. The data obtained from these experiments will be analyzed to further the understanding of high-pressure voidage-velocity relationships, flow-regime transitions, and the elevation of terminal velocities brought about by "particle clustering."

Table 31.
Parameters for
Bed Expansion Experiments

Pressure (atmospheres)	1, 16, 32, 64
Solids type	coal, glass spheres, alkalinized alumina
Solids size	fine (-200 + 325 mesh), medium (-100 + 200 mesh), coarse (-20 + 100 mesh)
Gas velocity (ft/sec)	0.0 - 3.0

Analysis of the data obtained in the pressure fluctuation experiments was begun. At this point, no conclusions have been drawn; however, the data agree favorably with atmospheric-pressure data obtained from the literature. Analysis will continue, with the objective of establishing mathematical relationships between pressure fluctuations and fluidized-bed characteristics, such as flow-regime transitions, bubble size, and bubble rise velocity.

The effort of Dr. L.-S. Fan, Ohio State University, was concentrated on setting up a photographic system for a two-dimensional fluidized bed and analyzing the voidage distribution in the bed. The photographic system included a still camera, a high speed motion picture camera, and the appropriate lighting fixtures. In order to determine bed voidages, colored particles that can be easily identified in the films were added to the bed. Local voidage fluctuations with time were determined based on a frame-by-frame analysis of the motion pictures. The x,y locations of the colored tracer particles were determined and recorded using a computer digitizer. At least twenty-five data points were taken for each square centimeter of the bed. These data were then processed in the computer to determine the x- and y-velocity components, total speed, average speed, variance, mean square velocity, etc. Similar experiments had been conducted by other researchers using monosized particles of different densities. In these experiments, the variance of local void fraction distribution increased as the liquid flow rate increased, while the variance of the distribution approached zero as the voidage approached one. The results of the experiments performed to date suggest that these relationships also hold true for a system of monodensity particles of different sizes.

Work on verification of a fundamental correlation for estimating minimum fluidization velocities at elevated pressures and temperatures was continued by Dr. W.-C. Yang, Westinghouse Electric Corporation. The fundamental nature of this correlation lies in the fact that it is based on a discrete particle model rather than a pipe flow analog. Having been successfully applied to a variety of data obtained from the literature, this correlation is believed to represent a valid fundamental approach to estimating minimum fluidization velocity at a wide range of pressures and temperatures. A more detailed discussion of the development of this correlation will appear in a forthcoming paper based on this work.

Treatment of Coal Gasification Wastewaters

*C.J. Drummond, 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. Supercritical Fluid Extraction

In this investigation, an innovative extraction process, employing supercritical fluids, will be developed for the treatment of coal gasification process wastewater. Certain compounds have a much greater solubility in supercritical fluids than they would in the same substance in its ordinary liquid or gaseous states. In order to determine the optimum conditions for the extraction of various contaminants from this wastewater using supercritical carbon dioxide, an apparatus consisting of a 1-liter, high-pressure, stirred autoclave; a 4-liter supercritical fluid accumulator; and associated instrumentation, tubing, sample bombs, and compressor is being constructed. This apparatus is to be operated in a batch mode to determine distribution coefficients for the contaminants in coal gasification process wastewater and in a semicontinuous mode to determine potential effluent quality and problems that might be encountered during continuous operation. The conditions chosen for the series of runs determining distribution coefficients are shown in Table 32.

B. Westinghouse Wastewater Steam 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 of the wastewater or discharge to the environment. This would provide a simple wastewater treatment system employ-

Table 32.
Experimental Conditions for Determining Distribution Coefficients

Run	Density, g/cm ³	Temperature, °C	Pressure, bar
1	0.50	45	1.04
2	0.60	45	122
3	0.70	45	146
4	0.80	45	200
5	0.50	60	133
6	0.50	70	150
7	0.50	80	175
8	0.50	90	200
9	0.70	50	159
10	0.70	55	180
11	0.70	60	200
12	0.85	35	200

ing steam stripping as the sole treatment operation. Results of analyses of this water are shown in Table 33.

Removal of contaminants from the wastewater will be optimized by varying the stripping-steam-to-wastewater ratio and the bottoms pH. Operation of the experimental system will be divided into two periods. Free-leg steam stripping will be investigated first at the pH of the raw wastewater. During free-leg stripping, stripping-steam-to-wastewater ratios from 0.5 to 2.5 lb of stripping steam/gal wastewater will be investigated. Subsequently, both the pH and the stripping-steam-to-wastewater ratio will be varied in the operation of the fixed-leg steam stripper. Conditions for these experiments will be determined contingent on the contaminants remaining after operation of the fixed-leg steam stripper.

C. 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.

Currently, an improved analytical preparation technique is being investigated. Residual solvent in the raffinate interferes with the deter-

Table 33.

Westinghouse Gasifier Wastewater	
Phenols	≤ 1 mg/L
COD	130 - 250 mg/L
TOC	120 - 340 mg/L
Total Ammonia	500 - 4000 mg/L
Sulfide	20 - 60 mg/L
Chloride	45 - 630 mg/L
Cyanide	30 - 55 mg/L
Thiocyanate	50 - 135 mg/L

mination of total organic carbon (TOC) and chemical oxygen demand (COD). The residual solvent stripping technique previously employed for these samples is not selective and caused significant scatter in the data.

Coal Flow Test Facility

M.P. Mathur, Cost Account Manager

*J.I. Joubert, Chief,
Combustion Technology Branch*

The primary objective of this study is to evaluate Southwest Research Institute's (SWRI) ESR/NMR mass flowmeter.

Preparations necessary for the evaluation of SWRI's ESR/NMR flowmeter at high pressures using the HP/CFTL system were completed. Evaluation tests using two coals were conducted during the period October 11 to October 22, 1983. The test matrix was revised somewhat to accommodate SWRI's request to run both coals.

The shakedown of the Petro-Carb system was completed on October 7, 1983. All the instruments, including the load cells, were calibrated and spanned (zero and maximum) properly. Auburn Monitors were also checked for zero and span by flowing coal through the line. The cross-correlator system was also tested for solid-velocity measurements.

The ESR/NMR flowmeter was installed in the horizontal section of the line. Electrical signals from various instruments were tested and sent to the computer. Data acquisition was modified to collect data in the fast acquisition mode (0.1 sec)

for transient studies. A new computer program to monitor the particle velocity from the cross-correlator operating at a fast rate was also written. Display on a TV screen of mass flow rate information obtained every second from the Auburn Monitors and load cells was also accomplished. Several coal flow trial runs were conducted to test the whole system. Personnel from SWRI arrived on October 11, 1983, to conduct the test. Tests were completed by October 22, 1983. All data obtained from various instruments were transmitted to SWRI by PETC, and the flowmeter was shipped back to SWRI. This concludes the activity of this project for this year.

ANALYTICAL CHEMISTRY SUPPORT

H.L. Retcofsky, Coordinator

Analytical chemistry support at PETC involves a variety of functions, including the following:

- The development and application of advanced analytical techniques and methodologies for the solution of problems associated with the utilization and conversion of coal.

- The 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 standard samples.

During the past quarter, use of the Analytical Chemistry Branch Laboratory Information Management System (LIMS) to prepare sample inventory status reports was initiated. More than 3,000 samples were submitted for analysis and were entered into the system during the three-month period.

PETC, in its capacity as the only source of standard samples for the calibration of Hardgrove Grindability equipment, supplied twenty-one sets of the standards to domestic and foreign laboratories.

The applicability of two new techniques, high resolution field desorption mass spectrometry

and mass spectrometry utilizing a supercritical inlet system, is being explored for the analyses of nondistillate material from coal conversion. The feasibility of using an automated ash fusion apparatus in place of the conventional system is also under consideration. Design of the automated apparatus for the distillation of coal-derived liquids at reduced pressure (modified ASTM D-1160) is complete, and construction is underway. Multiple peak-monitoring capability is being added to the Center's high resolution mass spectrometer.

Schiller Laboratories was awarded a contract to perform water analysis, and the first option of the Kenwill contract for vacuum distillations and elemental analyses was exercised. In addition, the University of Kentucky was awarded a contract for in situ X-ray diffraction measurements on catalysts during reduction.

A long-term goal of the Analytical Chemistry Support function is complete documentation of all routine analytical procedures used within the Center. Preparation of volume II of the PETC Analytical Methods Manual is in progress, and Volume I is now ready for internal review.

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, (4) perform standardized chemical and physical analyses on coal and coke in support of government research programs and coal purchases, and (5) act as a referee laboratory in disputes involving coal analysis.

Arthur Wells and Hyman Schultz visited the laboratories of Kenwill, Inc., in Maryville, Tenn., to evaluate their performance as backup Analytical Support Contractor. Based on observations and discussions at the laboratory and the results received from Kenwill, they were judged to be performing in a satisfactory manner. The first option of the Kenwill contract has been exercised.

An award was made to Schiller Laboratories of Ingomar, Pa., to perform back-up water analyses for PETC. To date, over 1300 analyses have been performed by Schiller Laboratories on PETC samples.

A study is in progress aimed at comparing an automated ash fusion apparatus with the standard ASTM ash fusion procedure. The study, which employs a reducing atmosphere, will determine the precision of the newer method and will also determine if a real difference exists between the two procedures. The automated procedure offers the possibility of reducing the manpower required to perform the analysis.

In an effort to optimize procedures for dissolving particles found in acid rain samples, portions of two samples collected during the Deep Creek experiment were filtered through 0.1- μ membrane filters, and the particles retained on the filters were characterized using Scanning Electron Microscopy (SEM). Use of the X-ray fluorescence attachment to the SEM showed the presence (in decreasing order of occurrence) of Al, Si, S, P, K, Ti, Ca, Fe, Cu, and Na in the particles analyzed. The most easily identifiable particles, when compared with photomicrographs in the literature, were those of ragweed pollen. Although some were found in the acid rain samples, ragweed pollen was the predominant particle found in the experimental blank collected at Deep Creek.

A collection station for acid precipitation was erected on Bureau of Mines property at Bruceton and will be used to collect samples for this project when permission to access the station is received from the Bureau.

During this quarter, 21 sets of Hardgrove Grindability Index standards were shipped to foreign and domestic coal users for the calibration of

equipment. Seventy-six bimonthly check samples from the coal analysis laboratory, and 32 check samples from commercial laboratories were exchanged to check procedures and equipment.

During the quarter, 1,307 coal samples were received for standard ASTM analyses, of which 1,145 were analyzed by our contractor laboratory, and 162 were analyzed in-house. One hundred and thirty-two coal samples were submitted to the contractor laboratory for reanalysis, and the results were compared for compliance with ASTM specifications for allowable differences in analyses between laboratories. In addition to the standard coal analysis, 3,588 other analyses were requested and 3,453 reported during the quarter.

During the next quarter, the first option on the Schiller Contract will be renewed. Methods for concentrating trace elements in acid rain samples will be explored. These will include freeze drying and liquid-liquid extraction.

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 453 analyses were performed, varying in complexity from quantitative near-infrared determination of phenolic OH in coal liquids to detailed low voltage high resolution mass spectrometry analyses of coal extracts. Major users of spectroscopic support services were projects associated with the indirect liquefaction and the Physical, Chemical, and Thermodynamic (PCT) properties program.

A contract was awarded at the University of Kentucky for in situ X-ray diffraction analyses of several Co-impregnated zeolite catalysts to be reduced at 350°C under hydrogen. The structure and size distribution of the Co crystallites in the reduced zeolites will be determined.

The applicability of two mass spectrometry techniques to the analysis of nondistillates will be evaluated. Preliminary contacts were made

with the Eastern U.S. Regional Mass Spectrometry Center regarding use of their high resolution field desorption mass spectrometry facilities and with Battelle Northwest Laboratories regarding their supercritical inlet mass spectrometer system.

Multiple peak-monitoring circuitry for the high resolution mass spectrometer at PETC has been delivered, and installation is being scheduled. This accessory will greatly improve the measurement of relative ion yields at selected masses in liquefaction products.

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 in Building 83 for 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, 477 samples were submitted for gas analysis; 477 were reported and there is no backlog. For the same period, 140 samples were submitted for simulated distillation by gas chromatography; 183 were reported and the current backlog is 62.

The Analytical Chemistry Branch is now reporting its sample inventory status based on information generated automatically by the Branch's Laboratory Information Management System. The system is now fully operational.

Preparation of the second volume of Analytical Methods at use at PETC has begun. The methods to be included have been selected and authors assigned.

Design and construction have begun on an automated apparatus for the application of a PETC-modified version of ASTM Method D-1160 to coal-derived liquids. The apparatus should improve operator productivity and method precision.

PUBLICATIONS AND PRESENTATIONS

Title	Author(s)	
Acid Rain	B.D. Blaustein	Presentation at a Graduate Seminar, University of Pittsburgh, Pittsburgh, Pa., November 22, 1983
Influence of Solvents on Coal Liquefaction	B.C. Bockrath	Presentation at a Graduate Seminar, University of Pittsburgh, Pittsburgh, Pa., October 25, 1983
Characteristics of Coarse Particle Fluidization at High Pressure	D.C. Chltester	Presentation at 1983 AIChE Annual Meeting and Diamond Jubilee, Washington, D.C., October 30 - November 4, 1983
Post Combustion Flue Gas Cleanup	R.J. Demski	Presentation to Chemical Engineering Students, University of Pittsburgh, November 8, 1983
Status of Coal Cleaning Technology in the U.S.	A.W. Deurbrouck	Presentation at First Workshop on Alternative Energy Resources and Development, New Delhi, India, November 9, 1983
Research in Physical Coal Cleaning	R.E. Hucko	Presentation at the Second Australian Coal Preparation Conference, Rockhampton, Australia, October 10-14, 1983
U.S. Government Research in Coal Preparation	R.E. Hucko	Presentation to the CSIRO Division of Energy Technology, Melbourne, Australia, October 18, 1983
Measurement of Particle and Slip Velocities in Coal/Gas Systems	M.P. Mathur G.E. Kilnzing*	Fluidization and Fluid-Particle Systems: Theories and Applications, AIChE Symposium Series, No. 222, Volume 79, 1983
Incorporation of Quinoline Into Coal and Coal-Derived Products	N.K. Narain B.R. Utz H.R. Appell B.D. Blaustein	Fuel, 62, 1417 (1983)
Comments on the Effects of Coal Particle Size Consist on Furnace Ash Deposition	Y.S. Pan	Fouling and Slagging Resulting From Impurities in Combustion Gases, edited by R.W. Bryers, Engineering Foundation, 1983

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Syngas Conversion and Chemisorption Studies on Metal-Zeolite Catalysts	V.U.S. Rao R.J. Gormley A. Shamsi R.R. Schehl R.T. Obermyer*	Presentation at DOE Indirect Liquefaction Contractors' Conference, Pittsburgh, Pa., October 12-13, 1983
Infrared Studies on the Acidity of Metal Impregnated ZSM-5	K.H. Rhee F.R. Brown D.H. Finseth J.M. Stencel	Zeolites, Vol. 3, October 1983, pp. 344-348
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Slurry Bubble Column Reactor Design for Fischer-Tropsch Synthesis	J.A. Ruether	Seminar at Ohio State University, December 1, 1983
Mass Spectrometry Studies of the H-Donor Potential and Heteroatom Distribution of Direct Liquefaction Products	C.E. Schmidt	Presentation at Analytical Characterization Group Meeting, Ames National Laboratory, Ames, Iowa, November 2, 1983
Slurry Bubble Column Dynamics	D.N. Smith	Presentation at Indirect Liquefaction Contractors' Conference, Pittsburgh, Pa., October 12-13, 1983
Bubble Behavior in a Slurry Bubble Column Reactor Model	D.N. Smith W. Fuchs R.J. Lynn D.H. Smith M. Hess*	Chemical and Catalytic Reactor Modeling, ACS Symposium Series, No. 237, 1983
Vibrational Spectroscopic Studies on Coal Conversion Catalysts	J.M. Stencel	Presentation at the Heterogeneous Catalysis Meeting of the Office of Basic Energy Sciences, Gaithersburg, Maryland, November 8, 1983
Vibrational Spectroscopic Studies of Coal Conversion Catalysts	J.M. Stencel	Presentation at Laval University, Quebec, Canada, November 10, 1983

*Non-DOE

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Dual Cobalt Speciation in CO/ZSM-5 Catalysts	J.M. Stencel V.U.S. Rao J.R. Diehl K.H. Rhee A.G. Dhere* R.J. DeAngelle*	Journal of Catalysis, 84, pp. 109-118, 1983
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Catalyst Testing for Two-Stage Liquefaction	R.E. Tischer G.J. Stiegel D.L. Cillo N.K. Narain	Presentation at DOE Direct Liquefaction Contractors' Conference, Pittsburgh, Pa., November 16-17, 1983
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First-Stage Dissolution Studies	B.R. Utz S. Friedman	Presentation at DOE Direct Liquefaction Contractors' Conference, Pittsburgh, Pa., November 16-17, 1983
Reactions of Vehicles and the Effect of Vehicle Properties in Short Contact Time Liquefaction	B.R. Utz S. Friedman B.D. Blaustein	Presentation at DOE AR&TD Liquefaction Contractors' Conference, Pittsburgh, Pa., October 18, 1983
Evaluation of Some Regenerable Sulfur Dioxide Absorbents for Flue Gas Desulfurization	R.J. Walker D.J. Wildman S.J. Gasior	Journal of the Air Pollution Control Association, Vol. 33, No. 11, November 1983
Carbonization	J.G. Walters	Presentation at a Graduate Seminar, University of Pittsburgh, Pittsburgh, Pa., October 18, 1983
Fractional Destruction of Liquefaction Products	R.P. Warzinski	Presentation at Direct Liquefaction Contractors' Conference, Pittsburgh, Pa., November 16-17, 1983
Coal Preparation	Wu-Wey Wen	Presentation at University of Pittsburgh, Pittsburgh, Pa., November 15, 1983

*Non-DOE

Title**Author(s)**

Development of an Analytical
Method for the Determination of
Organic Compounds in Fossil
Fuel Aqueous Leachates

C.M. White

DOE/PETC/TR-84-1, October 1983

Gas Chromatographic Retention
Characteristics of Nitrated
Polycyclic Aromatic Hydrocarbons

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R.M. Hoes*

Chromatographia, Vol. 17, No. 11,
November 1983, pp. 605-612

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