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DOE/FE-0002/2
VOLUME II OF II

DR. 770

FOSSIL ENERGY PROGRAM REPORT

UNIVERSITY ACTIVITIES

1 OCTOBER 1977 — 30 SEPTEMBER 1978

U.S. DEPARTMENT OF ENERGY
ASSISTANT SECRETARY FOR FOSSIL ENERGY

DECEMBER 1979

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VOLUME II OF II

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PREFACE

The Fossil Energy Program is now in its second year under the Department of Energy. This document describes the Fossil Energy-supported contract and project activity for FY 1978.

The United States relies upon fossil energy for more than 90 percent of its energy requirements — oil, gas, and coal bear the great majority of our energy burden. Our economy is based on an infrastructure heavily dependent upon the utilization of fossil fuels; however, consumption patterns do not correspond with our fossil energy reserves. The critically low level of our oil reserves with respect to consumption demands is a major reason why oil imports have risen so high. This situation must be corrected, and it is our mission to develop technologies that will help assure a dependable supply of economically viable and environmentally acceptable energy from our fossil fuel resources.

The primary thrust of the Fossil Energy Program is on coal — especially direct coal combustion and what can be done to increase the environmental acceptability of coal. We are concerned with developing cleaner technologies, and we are working on precombustion cleanup, fluidized-bed combustion, and post-combustion cleanup. Longer range technologies are being developed that will use coal more efficiently; for example, magnetohydrodynamics, fuel cells, and high-temperature turbine utilization. To combat the rising oil and gas prices and to avoid long-term supply shortages, another Fossil Energy priority is the development of a capability to produce synthetic fuels from coal. We are also engaged in a coal mining research and development program that focuses on increased mine productivity and workers' safety through the development of improved technologies.

Our activity in the petroleum and gas research areas is intended to complement efforts in the private sector, which are to be further stimulated by new pricing or Federal incentives. Our present enhanced oil recovery efforts represent a shift in emphasis toward longer range, high-technology development projects instead of numerous field demonstrations and tests. The enhanced gas program emphasizes activites to increase our knowledge of the size and economic productivity of the unconventional gas resources. We need to determine quickly whether this resource can be relied upon to fulfill a large portion of our future energy needs. We are also involved in oil shale development, with the major research concentration on in situ retorting.

We are continually assessing our program. Total annual funding has increased from $58 million in FY 1973 to $881 million in FY 1979. Fossil Energy is working closely with all parts of the Department of Energy, other appropriate Federal agencies, industry, and universities to insure that we maintain a balanced, aggressive, and responsive program that is suited to our national needs.

George Fumich, Jr.
Assistant Secretary
for Fossil Energy

FOREWORD

This report contains descriptions of each Fossil Energy Program contract and project. These descriptions are arranged in conformance with planning and budgetary documents. This Volume II is devoted to university contracts that are part of the Advanced Research and Technology Development Program, and it is arranged alphabetically by state. Other university contracts that are vital parts of specific programs appear in the appropriate technology areas, such as Liquefaction. A list of abbreviations and acronyms (p. 753), a glossary of terms (p. 763), and an index of companies and institutions (p. 767) are provided for reader convenience. Projects being conducted by Energy Technology Centers or National Laboratories are described at least quarterly in reports issued by these organizations. The results of contracts are reported at various intervals, depending on the type of contract, but at least annually. These reports are not listed individually in the "Publications" sections but are available from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161.

Readers interested in more information on program structure and planning are referred to the *Fossil Energy Program Summary Document*. The Department of Energy also publishes several abstract journals:

- Fossil Energy Update (monthly, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161)
- Energy Research Abstracts (biweekly, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402)
- Energy Abstracts for Policy Analysis (monthly, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402).

FOSSIL ENERGY ADVISORY COMMITTEE

The Fossil Energy Advisory Committee (FEAC) is comprised of individuals from industry in the energy-producing field, as well as the environmental, academic, and scientific communities, labor, consumer, and public interest groups. FEAC members are appointed every 2 years by the Program Director for Fossil Energy and serve under his chairmanship. This blend of technical research capability, executive, and practical experience in all aspects of fossil energy activities has enabled the Committee to render expert counsel in the problem and opportunity areas involving fossil energy RD&D and the environment. Thus, because of this unusual combination of expertise, the Department of Energy's Fossil Energy Program has access to invaluable guidance in the direction, conduct, and application of its program.

Meetings are held three times a year. Two of these meetings are held in Washington, D.C., and one is held at project sites in various parts of the United States. A Committee meeting was held on April 14, 1977, in Washington, D.C., to discuss the role of the Environmental Protection Agency and the Council on Environmental Quality with respect to the Fossil Energy Program. Also considered were the Fossil Energy Environmental Development Plans, Fiscal Year 1978 Budget, analytical efforts in support of coal-derived electric utility, and industrial fuels strategy.

FEAC met again on August 25, 1977, in Morgantown, West Virginia, and focused on the Market Oriented Program Planning Study (MOPPS), the structure and status of the Department of Energy, the overview of fluidized-bed combustion, and hot-gas cleanup technology.

In January of 1978, the Committee met in Washington, D.C., and discussed MOPPS, shale oil, and tar sands. During that meeting, the Committee also engaged in discussion of ways the Nation could meet the President's goal of lowering imports to 5.8 million barrels per day by 1985. The next Committee meeting was held September 21, 1978, in Laramie, Wyoming, at which the members discussed oil shale technology and underground gasification of coal. Environmental and commercialization concerns relating to oil shale were also considered. In addition, extensive comments and recommendations were made by the Committee members on the DOE synfuels program and hot-gas cleanup technology.

The Executive Secretary for the Committee is Dr. G. Alex Mills, Acting Director, Office of International and Scientific Programs. Mrs. E.B. Frazier of the Division of Planning and Systems Engineering is the FEAC Program Officer.

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UNIVERSITY ACTIVITIES

The nation's universities, during FY 1978, continued to play a significant role in the advancement of fossil energy technology. A constant interchange of information provided universities with a better understanding of fossil energy problems and needs for research. As in the past, Fossil Energy sponsored several faculty and student participation programs and teacher workshops and institutes. Approximately 400 projects were active during FY 1978 in the areas of gasification, liquefaction, materials and components, oil, gas, shale, in situ technology, and magnetohydrodynamics. Funds provided for university projects totaled $35.8 million. Significant achievements include the following:

- A variety of models were generated for underground coal gasification aimed at predicting product gas composition, sweep efficiencies, and the nature of roof collapse by the University of Wyoming, West Virginia University, and the University of Texas

- Research at the City University of New York indicates that titanium hydride, when added to coal prior to flash hydrogenation, markedly increases the yield of hydrocarbon liquids

- Auburn University has demonstrated that treatment (prior to recycling) of coal-derived mineral residue can drastically reduce the amount of hydrogen required for SRC processing

- Research at the Colorado School of Mines has demonstrated that gas-phase hydrogen generated by chemical reaction of carbon monoxide and steam is as effective as pure hydrogen in promoting the rate of coal liquefaction

- Researchers at the University of Tennessee have found new approaches to control NO_x in MHD processes

- Pennsylvania State University has discovered novel synthetic procedures for preparation of surfactants and co-surfactants for enhanced oil recovery, using a wide variety of petroleum fractions

- The Massachusetts Institute of Technology has developed new methods for modeling the physical phenomena occurring in a fluidized-bed combustor.

As is evident, university scientific and technical expertise is an invaluable asset to the Fossil Energy Program both for performing energy-related research and also for training young people to meet future energy demands.

COAL LIQUEFACTION WITH APPLICATION TO SRC AND RELATED PROCESSES

AUBURN UNIVERSITY
DOE - \$741,222; Auburn U - \$318,581
7/1/76 - 11/1/78
Principal Investigators - J.A. Guin, A.R. Tarrer

OBJECTIVES – The purpose of this project is to provide an increased fundamental understanding of Solvent Refined Coal (SRC) process chemistry as well as to provide guidelines and recommendations leading to economical and technical improvements in SRC technology through systematically investigating, characterizing, and delineating the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes. Specific problem areas being investigated include the effects of solvent and coal types as well as processing conditions upon coal particle dissolution; the effects of process variables, mineral matter content, and reactor configuration upon coal conversion, hydrogenation, and heteroatom removal rates; and the detailed characterization of SRC recycle solvents and products by gas and liquid chromatography. These studies are valuable in selecting improved economic operating conditions and flow schemes for the SRC process, in providing an extended map of the process variable space, and in determining process kinetic models for future optimal design and scale-up to commercial-sized plants.

RECENT WORK AND ACCOMPLISHMENTS – A new short-residence-time catalytic two-stage SRC process has been developed to produce a low-sulfur SRC by improving selectivity for hydrodesulfurization over hydrogenation. The process will meet the more stringent new point source emission standards (NPSES) (0.5 to 0.6 percent sulfur) proposed by the Environmental Protection Agency (EPA). In the first stage of the process, residence time and hydrogen consumption are minimized through the use of inexpensive mineral catalysts (e.g., SRC residue ash, coal ash) that have been treated to improve their selectivity for desulfurization over hydrogenation. The second stage of the process involves hydrotreating the filtered reaction mixture with a commercial Co-Mo-Al catalyst. Selectivity for desulfurization in two-stage hydrodesulfurization of coal can be improved by using low reaction temperatures, short residence times, the ash of SRC residue as a first-stage catalyst, and Co-Mo-Al as a second-stage catalyst. Two-stage catalytic SRC processing has been observed to be more selective for desulfurization than (catalytic or noncatalytic) single-stage SRC processing. Other accomplishments are: coal particle size measurements by Coulter Counter analysis have been related to filterability in the SRC process; there is little effect of agitation rate on the dissolution of coal, but it is significant for the transfer of gaseous hydrogen to the solvent; the effect of pretreatment of coal with NaOH and $Fe_2(SO_4)_3$ solution, or by grinding in hydrogen donor solvent on conversion and sulfur removal in liquefaction has been determined; there is strong involvement of coal minerals in rehydrogenation of solvent and in hydrogenation of coal-derived liquid products such as oils, asphaltenes, and presasphaltenes; significant catalytic activity of coal minerals in heteroatom removal of model compounds (S-, N-, O- compounds) has been observed; coal dissolution and hydrogen transfer kinetics has been found to follow a second-order consecutive reversible reaction; the separation and characterization of SRC by gel permeation chromatography and high-pressure liquid chromatography has been achieved; and implementation of various analytical techniques—including FTIR, X-ray fluorescence, and gas chromatography—has been accomplished.

PLANS FOR THE COMING YEAR – Work will continue on coal particle dissolution studies, reaction kinetics and process variable studies, and implementation of new analytical techniques. Particular emphasis will be placed on studying major factors for better solvent quality in the SRC and related liquefaction processes by determining the individual major structural groups present in the process solvent through using various analytical techniques such as FTIR and NMR; characterization and preparation of coal minerals and determination of major constituents responsible for their catalytic activity and selectivity in order to develop new active mineral catalysts and to understand basic principles in coal mineral catalysis; model compound studies to evaluate the relative catalytic activity and selectivity of coal minerals in heteroatom removal; application of better analytical techniques for characterizing SRC and coal-derived products; and mapping studies of the process variable space for modeling and optimizing the SRC reactor.

INTERNATIONAL CONFERENCE ON INDUSTRIAL APPLICATIONS OF MAGNETIC SEPARATION

AUBURN UNIVERSITY
DOE - $6000; Cosponsors* - $19,000
8/1/78 - 2/1/79
Principal Investigator - Y.A. Liu

OBJECTIVES – The purpose of this conference project is to provide unique opportunities for researchers and practitioners to exchange the latest information on R&D in magnetic separation, emphasizing the existing and potential industrial applications of magnetic separation to the important areas of coal desulfurization, mineral beneficiation, resource recovery, water treatment, particulate control, and chemical processing. The conference was also intended for the participants to discuss and identify the research needs and opportunities leading to new industrial applications of magnetic separation.

RECENT WORK AND ACCOMPLISHMENTS – A 4½-day meeting entitled "International Conference on Industrial Applications of Magnetic Separation" was held at Franklin Pierce College, Rindge, New Hampshire, on July 30-August 4, 1978. The conference was cosponsored by the Engineering Foundation, Auburn University, and IEEE Magnetics Society; and supported by grants from five industrial and governmental organizations, including DOE. It was attended by 110 invited participants from the U.S. and 10 foreign countries, including Bolivia, Canada, Finland, France, W. Germany, Israel, Japan, Norway, Sweden, and United Kingdom. These participants were believed to represent essentially all active university, industry, and government R&D groups, as well as major equipment users and manufacturers in magnetic separation throughout the free world. The conference program consisted of 42 papers presented in eight technical sessions and an informal research workshop. The proceedings of the conference have been edited by the principal investigator and should not only represent a state-of-the-art reference in the field of magnetic separation, but also provide interested scientists and engineers some definitive recommendations regarding future R&D work leading to new industrial applications of magnetic separation.

PLANS FOR THE COMING YEAR – This project was completed in January 1979. Copies of the proceedings will be published in April 1979 as a 210-page monograph entitled, *Industrial Applications of Magnetic Separation*. It will be available as IEEE Publication No. 78 CH1447-2 MAG from the IEEE office, 345 East 47th Street, New York, New York 10017.

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*Cosponsors and their contributions are as follows: Electric Power Research Institute - $3000; Engineering Foundation - $3000; Gulf Oil Foundation - $1000; and National Science Foundation - $12,000.

FEASIBILITY STUDIES OF IN SITU COAL GASIFICATION IN WARRIOR COAL FIELD

UNIVERSITY OF ALABAMA
DOE - $22,000; Other Sources - $60,000
10/1/77 - 9/30/78

OBJECTIVES – The objective of these feasibility studies is to determine whether in situ gasification is technically feasible for seams of Eastern bituminous coal less than 3-ft thick. There are large reserves of such seams in the Warrior coal field of West Alabama that are not recoverable by conventional mining techniques. If the energy in these coal seams could be recovered in the form of a low-BTU gas, ample use could be found for it in the industries in Birmingham and other manufacturing centers of northern Alabama.

RECENT WORK AND ACCOMPLISHMENTS – Experiments have been conducted in both forward and reverse combustion utilizing narrow cracks in the coal as air passages. Single cracks as well as multiple cracks were tested. Tests of forward combustion in virgin coal were not successful because of the swelling nature of the bituminous coal. Reverse combustion tests showed that the reaction will proceed satisfactorily if multiple cracks are available so that sufficient surface area is available. Reverse linking will, thus, be necessary in bituminous coal seams even though hydraulic fracturing is used to prepare the seam. The tests also show that some char will remain in the reaction zone. The extent of the pyrolyzed region is of interest, and further tests on shrinking core models, char properties, and heat transfer within the coal seam will be used to attack this problem. An additional combustor has been fabricated from 2-in. diameter stainless steel that will be used in conjunction with a tube furnace to investigate the effects of water influx on gas quality during forward combustion of char. Previous shrinking core model studies have shown that air and gases will not flow through the char itself, but must flow through cracks or channels around the char particles. Ash buildup on the char particle provides a diffusion barrier that inhibits continued reaction. The tendency for the char in the burned-out zone to continue to react during reverse combustion will be a function of the ash thickness, oxygen content of the air, and heat-transfer characteristics of the char and ash. An experimental apparatus is now in use to determine the relative importance of these factors. A systematic survey of the literature regarding coke and char properties is being conducted. Experimental apparatus for investigating the thermal conductivity and reactivity has been constructed and tests are underway.

A study was made of gas evolution during pyrolysis of a highly swelling medium-volatile bituminous coal from Alabama. The gas evolution was studied by a thermovolumetric method convering the temperature range from ambient to 1000°C at a heating rate of 3°K/min. The experiments were designed to give a direct comparison of Gwin-seam coal with Roland-seam subbituminous coal studied by Campbell. The amount and rate of evolution of H_2, CH_4, C_2H_4 and C_2H_6, and C_3H_8 from Gwin-seam coal matched closely those of the Roland-seam coal at corresponding temperatures. The amounts of CO and CO_2 were much less than for subbituminous coal, but were found to be proportional to the amount of oxygen in the original coal. These studies indicated no difference in the gas evolution during pyrolysis that could cause a significant difference in the performance of the coals during gasification. In the study on thermal conductivity of strata near the Gwin seam, measurements were made on core samples of overburden strata over a temperature range of 200° to 1200°F. The results are considered adequate for future heat-transfer analysis Coal samples from the Blue Creek seam of the Warrior coal field were pyrolyzed to temperatures ranging from 200° to 1360°C. The weight loss of the coal was found to occur in the plastic region of 400° to 500°C. The coal was allowed to expand freely, and it was found that the expansion took place entirely normal to the bedding plane. The porosity of the samples was measured using a Washburn-Bunting porosimeter. Although widely scattered, the mean porosity of the unconfined coal pyrolyzed between 200° and 1360°C was 64.4 percent as compared to 7 percent as compared to 7 percent for the virgin coal. The porosities of several samples of coke from the laboratory combustor ranged from 9 to 32 percent, indicating that confinement of the samples during pyrolysis has a large effect upon porosity. Air permeability measurements revealed that most samples showed a positive deviation from Darcy's law. The permeability data were best correlated by White's power law model. The data were quite scattered, but the data indicated that the permeability of the coke is not high enough to account for the air rates and pressure drops encountered in laboratory or field tests. The most probable mechanism of flow is through cracks in the coal or coke.

PLANS FOR THE COMING YEAR – Work will continue on the 2-in. combustor using water injection in forward combustion. Gas quality as a function of water rate and air rate will be studied. Experimental work on char reactivity and thermal conductivity will continue. Heat conduction away from the reaction zone will be examined via numerical means. The results of the char property studies will be used. Work on the shrinking core model will continue.

RECONNAISSANCE AND PROCESSING OF IMPOUNDED COAL WASTES

UNIVERSITY OF ALABAMA, MINERAL RESOURCES INSTITUTE
DOE - $367,080
9/16/78 - 9/15/80
Principal Investigator - J.S. Browning

OBJECTIVES – The objective is to sample, test, and analyze coal impoundments in Alabama to determine the total quantity of coal, the quantity of recoverable coal, and the quality of recoverable coal in each impoundment. The sampling and testing procedures should be applicable to impoundments in other coal-producing states. A second objective is to sample the washery wastes discharging into the impoundments as a means of evaluating the quantity and quality of such wastes.

RECENT WORK AND ACCOMPLISHMENTS – A program has been developed for sampling the waste fine coal being discharged from each of the 26 coal preparation plants operating in Alabama to evaluate the quantity and quality of such coal. Six plants have already been sampled, and it is anticipated that the sampling will be completed during the second quarter of FY 1979. The type of drill rig necessary for obtaining accurate samples of the waste fine impoundments has been determined. Requests for bids on the drilling equipment have been sent to various companies. With the data obtained from earlier sampling of waste coal impoundments in Alabama and from laboratory tests to recover coal, capital and operating costs have been developed for recovering coal from the waste impoundments in a plant having an hourly capacity of 170 tons. Construction cost of the plant is estimated at about $1,113,000. The capital cost (all costs based on 1978 price quotations) includes equipment, freight, equipment installation, building construction, and all other accessory installations necessary to place the plant in operation. Based on the data obtained from pilot plant tests, the direct operating cost for preparation of the waste fine coal in a plant of 170-t/hr is estimated to be $1.68/t of material treated.

PLANS FOR THE COMING YEAR – Almost all coals when washed or cleaned produce considerable fine material consisting of clay plus fine particles of rock and coal. These fines (called sludge) along with waste were discharged into large impoundments. Although some washing plants include circuits for recovering the fine coal, most continue to discharge fine coal and waste into impoundments, some of which contain as much as several million tons of waste averaging 50 to 75 percent coal. This coal is an important resource that can be recovered at low cost. Furthermore, the volume of the impoundments could be reduced by 50 to 75 percent if the coal were recovered, thus reducing the safety hazard of the ponds and their degrading effect on the environment. A previous survey of impoundments in Alabama showed 28 in the size range of 350,000 to 2,000,000 tons. These tonnage estimates were very rough so a more comprehensive sampling and estimating program has been planned. The volume of each impoundment can be calculated reasonably well using a U.S.G.S. or comparable contour map and a plane table type survey of the impoundments. Each impoundment will be sampled by drilling cased holes spaced on a 100-ft grid for the larger impoundments and 50-ft grid for the smaller. Corings from each hole will be separated into 10-ft intervals from the surface to the bottom and subjected to sink/float tests to determine the quantity and quality of the coal and to provide information on the amount of recoverable coal depending on the process employed. This pilot study is to develop a satisfactory method for calculating tonnages, sampling the impoundments, and testing the samples. If successful, the methodology will be followed in determining the quantity and quality of coal contained in impoundments of other coal-producing states.

DEHYDRATION OF ALASKAN COALS FOR BETTER UTILIZATION

UNIVERSITY OF ALASKA
DOE - $24,672; Alaska U - $1299
9/1/78 - 8/31/80
Principal Investigator - P.D. Rao

OBJECTIVES – The program objectives and scope of research include: measuring mechanical strength of coal in relation to sample orientation with reference to bedding plane, size of test piece, and coal characteristics, all determined with inherent bed moisture; study of dehydration by means of various mechanisms using geometrically shaped pieces, the processes to include among others, conventional heat drying at atmospheric pressures, high-pressure drying, and hot oil immersion; characterization of the dried test pieces as to their mechanical strength, fracture pattern, retained moisture, and moisture reabsorption; amenability of the dried products to oxidation and spontaneous combustion; studies on prevention of moisture reabsorption of the dried products; relation of shrinkage cracks and fracture pattern to petrography and coal characteristics; establishment of a research program on drying for better utilization of Alaskan coals; and characterizing products released during drying process.

RECENT WORK AND ACCOMPLISHMENTS – Coal samples have been collected in large pieces from No. 4 seam, Lower Lignite Creek, Usibelli Coal Mine. This seam has the largest proven and potential coal reserves in the Lower Lignite Creek area. A system of holding coal pieces and cutting 1¼-in. cores has been built, and several pieces of cores have been cut for preliminary investigations. A high-pressure-high-temperature dehydration system on order has been delayed because of a heavy workload in the supplier's shops.

PLANS FOR THE COMING YEAR – After receipt of the dehydration system from the supplier, this project will be fully operational. Completion of the objectives by September 20, 1979 is not anticipated and may need to be extended for 1 year.

PETROGRAPHIC AND MINERALOGICAL CHARACTERIZATION OF ALASKAN COALS

UNIVERSITY OF ALASKA
DOE - $18,108; Alaska U - $3277
7/11/78 - 7/10/79
Principal Investigator - P.D. Rao

OBJECTIVES – The objectives of this investigation are to determine: petrographic composition and reflectance rank of 12 coal samples, and sink-float fractions of 3 coals; minerology of 12 raw coals and sink-float fractions of 3 coal samples after ashing in a low-temperature asher; and chemical composition of ash of 12 raw coals and 3 sink-float fractions, by atomic absorption and emission spectrochemical methods.

RECENT WORK AND ACCOMPLISHMENTS – Samples from the following areas have been collected and processed:

UA No.	Location	Characterization
100	No. 6 seam, top 3.2 ft	Raw coal
101	No. 6 seam, middle 18.3 ft	Raw coal
102	No. 6 seam, lower 3.3 ft	Raw coal
103	Moose seam	Raw coal
104	Caribou seam	Raw coal
105	No. 2 seam	Raw coal
106	Mine seam, Jarvis Creek Field	Raw coal
107	Castle Mountain Mine	Sink-float
108	Premier Mine	Raw coal
109	Kuk River, Wainwright	Raw coal
110	Meade River	Raw coal
111	Broad Pass	Raw coal
112	Little Tonzona River	Raw coal
113	Beluga Field	Sink-float
119	No. 4 seam, Usibelli Coal Mine	Sink-float

The following work has been completed on the samples: raw coals and sink-float fractions were crushed at 20 mesh and pelletized with thin and polished sections to be made of them; pulverized-60 mesh samples have been ashed at 450°C and are now being analyzed for major, minor, and trace elements; and a fluorescence microscope has been ordered, and the petrographic work will commence after receipt of the microscope. The low-temperature asher has not been operating satisfactorily and has been shipped to the manufacturer for repairs.

PLANS FOR THE COMING YEAR – Petrographic work will begin after receipt of the fluorescense microscope and ashing, and mineralogical analyses will be undertaken after receipt of the asher. It is anticipated that the project will be completed by July 1979.

CHARACTERIZATION AND EVALUATION OF WASHABILITY OF ALASKAN COALS

UNIVERSITY OF ALASKA
DOE - $24,953; Alaska U - $2773
3/1/78 - 2/1/79
Principal Investigator - P.D. Rao

OBJECTIVES - The objectives are to sample 12 coal seams from various coal fields of Alaska; crush the samples to 38mm, 10mm, and 14 mesh and separate 38mm by 100 mesh, 10mm by 100 mesh, and 14 mesh by 0 samples at 1.3, 1.4, and 1.6 specific gravities; analyze the products for ash, moisture, heating value, total sulfur, and pyritic sulfur; and determine proximate and ultimate analysis and hardgrove grindability of raw coals.

RECENT WORK AND ACCOMPLISHMENTS – The following samples were collected:

UA No.	Location
109	Wainwright, Northern Alaska Field
110	Meade River, Northern Alaska Field
111	Broad Pass Field
112	Little Tonzona Field
113	Beluga Field
114	Sagwon Bluff
115	Yentna Field, lower
116	Yentna Field, upper
117	Tramway Bar
118	Cabin Bed, Kenai Field
119	No. 4 seam, Nenana Field

Washability studies on all samples, analysis on all raw coals and sink-float products, and the project itself is complete in all respects. The final report is being prepared.

PLANS FOR THE COMING YEAR – A proposal has been submitted to sample 15 coal seams on an 18-month grant. These samples will be processed as before for washability and raw coal characterization.

HIGH-PRESSURE STIRRED NEAR-PLUG-FLOW LABORATORY REACTOR

UNIVERSITY OF ARIZONA
DOE - $41,081
8/15/77 - 8/14/79
Principal Investigator - D.H. White

OBJECTIVES — The overall objective is to develop a high-pressure stirred near-plug-flow laboratory reactor, capable of handling more dense and more viscous coal slurries over a wider range of flow velocities than possible in a conventional unstirred tubular reactor. Tubular reactors are limited in their degree of mixing and approach to plug flow, requiring high turbulence and reasonably dilute, less viscous slurries. The objective is believed feasible by modifying a plasticating extruder, which exhibits the desired characteristics. Thus, the objectives of the first year of this project involved modifying an existing polymer plasticating extruder for operation upon dense coal slurries in oil, developing auxiliary operating procedures, obtaining operating data to determine reactor feasibility, and making recommendations on reactor design.

RECENT WORK AND ACCOMPLISHMENTS — An existing plasticating extruder, complete with instrumentation and data logging by a minicomputer, was modified by adding pressure slurry feed, redesigning existing screws, and providing certain sampling and safety devices. The unique character of flow of the extruder was retained; namely, handling a dense slurry, generating pressures to more viscous liquids and slurries, providing internal mixing by the screw, and maintaining this flow in a near-plug condition as proven by its narrow residence time distribution (RTD). Operating data were obtained on the performance of the modified extruder for handling coal/oil slurries including concentrations, pressure and temperature profiles along the screw, RTD by radioactive tracer technique to determine the closeness to plug flow, the degree of internal mixing by RTD correlations, and experiments on axial dispersions and some laboratory rheological properties of the slurries utilized. Coal/gear oil slurry concentrations up to 60 weight percent coal were handled without difficulty. Recommendations were made upon the design of a laboratory reactor based on these results.

PLANS FOR THE COMING YEAR — Based on these results, a laboratory reactor is being designed and will be constructed during FY 1979.

SAMPLING AND ANALYSIS OF SMALL PARTICLES FROM HOT PROCESS STREAMS

UNIVERSITY OF ARIZONA
DOE - $44,675
9/1/78 - 8/31/80
Principal Investigator - T.W. Peterson

OBJECTIVES — This research project is designed to provide a comparison among various techniques for measuring or inferring particle-size distributions in hot process streams. The techniques to be studied include conventional extractive techniques (optical particle counter and cascade impactor studies), in situ laser light-scattering studies, and theoretical correlations based on computer-simulated particle physics. The techniques will be developed and tested on a bench-scale hot-particle generator and calibrated initially with particles of known size. The purpose for this work is to develop a means for sampling hot particles that will be useful in studying pulverized coal combustion processes, coal-fired magnetohydrodynamic units, and fluidized-bed combustors, to name a few.

RECENT WORK AND ACCOMPLISHMENTS – All work performed has been preliminary. In the first phase of this program, the hot-particle generator configuration has been designed. Materials for construction are being ordered, as are particle standards for calibration of the system. On site is all instrumentation necessary to perform conventional analysis by extractive techniques.

PLANS FOR THE COMING YEAR – After construction of the hot-particle generator, the sampling system will be calibrated with particles of known size by means of an optical particle counter, against which both laser and theoretical modeling techniques can be tested. Initial calibration runs will be performed with the cascade impactor and optical particle counter in early June 1979.

POLLUTANT CONTROL THROUGH STAGED COMBUSTION OF PULVERIZED COAL

UNIVERSITY OF ARIZONA
DOE - $165,052; Arizona U - $14,353
4/24/75 - 10/24/78
Principal Investigator - J.O. Wendt

OBJECTIVES – The purpose of this program is to define the salient mechanisms of NO_x formation during pulverized coal combustion and to determine optimum staging configurations for low NO_x emissions. Because increased use of coal for combustion will lead to unacceptable increases of NO_x emissions without application of some kind of pollutant abatement technology, it is important to determine any limitations set by coal composition, temperature, and stoichiometry to pollutant control through combustion modifications. Combustion modifications, such as staging, have the potential of achieving low NO_x emissions at a cost of one order of magnitude less than that of instack NO_x removal.

RECENT WORK AND ACCOMPLISHMENTS – The final year of this contract has determined that the slow rate of NO destruction in the first stage will limit staging effectiveness under classical staged conditions. Staging effectiveness is strongly influenced by coal composition and heat loss in the first stage. Low NO emissions after staging can best be achieved through a rapid temperature quench from a high initial temperature in the first fuel-rich stage. Coal composition effects are determined by the rate at which nitrogen is devolatilized relative to those at which local oxygen is consumed by the non-nitrogeneous species. Some, but not all coals allow subsequent reduction of NO at fuel-lean conditions after staging, and this characteristic can be used to obtain low NO emissions from the burning of appropriate coals. This research has also led to two potentially patentable ideas for increasing staging effectiveness: first, conducting staged combustion in three or more steps (advanced staging), which was demonstrated to lead to exhaust NO values of less than 100 ppm without excessive hot fuel-rich residence times; second, injecting a supplemental fuel into a slightly fuel-rich first stage to allow more rapid reduction of NO and XN species in that stage. Further work will be required before these techniques can be implemented in practice.

PLANS FOR THE COMING YEAR – This contract will be terminated in October 1978.

GASIFICATION OF RESIDUAL OIL IN MOLTEN PHOSPHATES

CALIFORNIA INSTITUTE OF TECHNOLOGY
DOE - $98,300
10/1/78 - Continuing
Principal Investigator - G.R. Gavalas

OBJECTIVES – The objective of this work is to demonstrate the feasibility and determine the kinetics of residual oil conversion to synthesis gas in a molten phosphate medium. Specific objectives include building a ceramic reactor able to contain the molten phosphate at temperatures 800^{o} to $1100^{o}C$ in which the steam-carbon and oxygen-carbon reactions can be carried out. Another objective is to study the kinetics of the reaction of several gaseous hydrocarbons and suspended coke particles with steam and oxygen. Finally, it is planned to develop a theoretical understanding of these processes by analyzing the interaction between relevant chemical and transport processes.

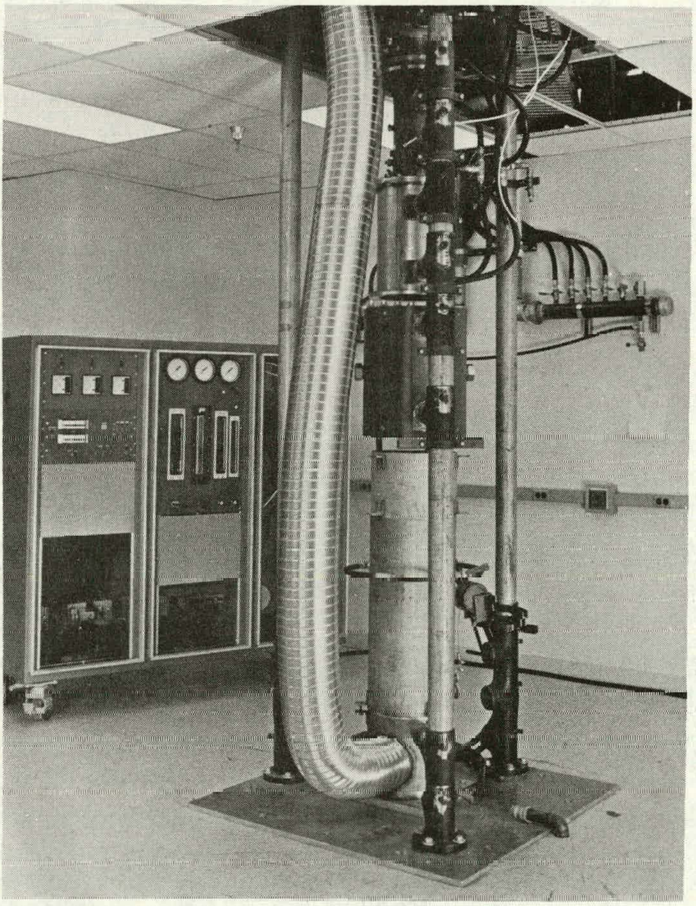
RECENT WORK AND ACCOMPLISHMENTS – The overall experimental system consists of a steam supply, reactor assembly, and analytical equipment. A steam-supply system has been constructed consisting of a preheater, a steam generator, and a surge tank. The preheater and the generator are controlled separately and, in conjunction with the surge tank, provide a smooth flow rate of steam. Two small-scale experiments have been conducted using a furnace and other existing facilities for studying molten salt reactions: contact angle and small-reactor experiments. The contact angle experiments consisted of melting the salt in a quartz container and placing a slab of graphite in the salt. The contact angle was measured when the surface remained horizontal upon intersecting the rod (Adam and Jessop procedure). The contact angle was observed visually as well as photographed. Measurements indicate a contact angle of molten sodium phosphate at its eutectic composition with graphite of 125 degrees ± 5 degrees. The small-reactor experiments used a 9-in.-long, 2-in.-I.D. mullite-crucible reaction vessel. Graphite was segregated so that it could not come into direct contact with the reactant gas bubbles. Air was used as the reactant, and the reaction observed was the conversion of carbon to carbon dioxide and monoxide. The predominant product was CO_2 with CO production consistently negligible (less than 0.01 percent of the product gas mixture). These experiments were addressed to distinguishing between the following two mechanisms: an intermediate species serves as the carrier of oxygen from the air bubbles to the graphite surface, and dissolved oxygen reacts directly with the graphite. Sodium sulfide was added to the salt as a possible oxygen carrier in an oxidation-reduction mechanism between sulfide and sulfate forms. No perceptible change in the rate was noted in adding up to 2.18 percent Na_2S as compared to pure sodium phosphate. It is still possible that another liquid species allows the first mechanism to operate.

PLANS FOR THE COMING YEAR – After completion of the construction and testing of the reactor assembly and the overall system, the first set of experiments will be the steam reforming of pure hydrocarbons. Then, the reactions with steam and air of finely divided coke or soot in the melt will be studied. The emphasis in these two classes of experiments will be to delineate reaction mechanisms and study the effect of fluid mechanical variables such as flow rates and solids loading on the gas holdup and interfacial area.

PULVERIZED COAL COMBUSTION

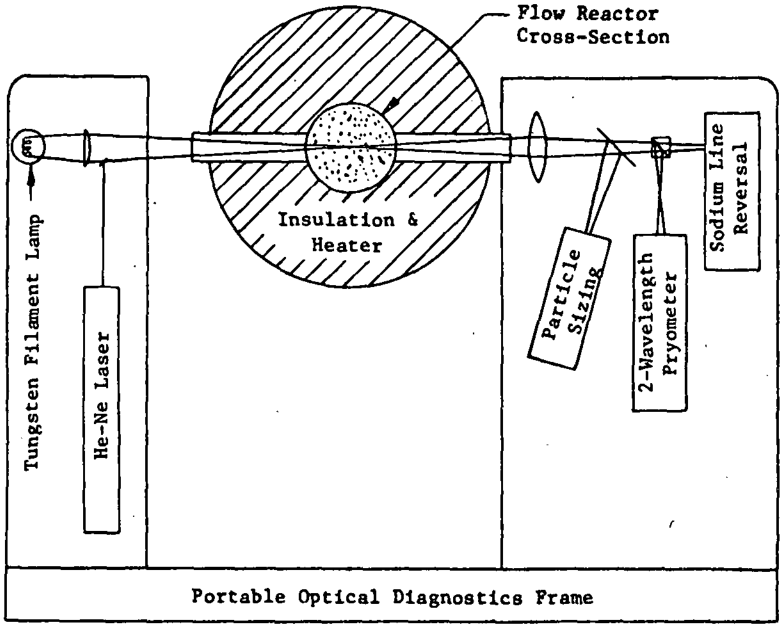
STANFORD UNIVERSITY
DOE - $150,000
7/1/77 - 6/30/79
Principal Investigator - C.H. Kruger

OBJECTIVES – The objectives of this research are to determine experimentally mechanisms and rates of pulverized coal particle combustion. Specific objectives are: development of an integrated high-temperature flow reactor and measurement system that is designed to give maximum accuracy in the experimentally determined pulverized coal reaction rates; application of the flow reactor system to determine reaction rates for representative coals burned under fuel-rich conditions ranging from 50 to 100 percent stoichiometric air; investigation of physical effects, including ash melting and particle breakup, on the primary mechanism of combustion and the resulting effect on coal reaction rates.



Flow Reactor Facility and Control Panel

RECENT WORK AND ACCOMPLISHMENTS – The design and construction of the flow reactor facility is nearly complete. Preliminary tests have been performed with the arc jet and upper stages of the flow reactor along with a new control panel facility that have demonstrated the feasibility of attaining the required temperatures in the flow reactor with some modification of the upper plenum stages to minimize heat losses. A satisfactory coal feeder technique has been tested, and construction of a scaled-up version is nearly complete. A unique optical diagnostics rig has been designed and fabricated with initial calibration and checkout scheduled for early February. This integrated rig will provide simultaneous, nonintrusive particle-size, temperature, and mean velocity measurements along with gas temperature measurements. These measurements are to be coupled with conventional probe sample measurements of product gas and remaining unburned char to provide sufficient data for a fundamental characterization of coal reactivity.



Plan View of Flow Reactor Diagnostics

PLANS FOR THE COMING YEAR – By April 1979, initial reactivity measurements of a subbituminous Montana coal in the range of 1600 to 1700 K will have been completed; then, the range of reaction temperatures will be extended up to 2000 K. At these higher temperatures, the gasification reactions with steam and CO_2 will be studied along with physical effects of particle fragmentation in the char burnout phase. Characterization of remaining fly ash properties after burnout will be obtained, including in situ measurements of fly ash size and number density, chemical composition, and particulate structure.

DEW POINTS OF HOT GASES FROM COAL GASIFICATION PROCESSES

UNIVERSITY OF CALIFORNIA, BERKELEY
DOE - $119,542
6/1/76 - 5/31/79
Principal Investigator - J.M. Prausnitz

OBJECTIVES – The long-range purpose of this research is to obtain fundamental physico-chemical data that, when coupled with theoretical results from molecular thermodynamics, will enable calculation of dew points in tar-containing gas mixtures at advanced temperatures and pressures.

RECENT WORK AND ACCOMPLISHMENTS – Theoretical work involves first a gas-phase equation of state appropriate to mixtures containing a variety of components. A suitable form for this equation of state has been established; it is the virial equation with virial coefficients calculated by a particular form of the square-well potential. This equation gives gas-phase fugacity coefficients needed for dew-point calculations. Square-well parameters have been established for calculating second virial coefficients for mixtures containing hydrogen, nitrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, light hydrocarbons, water, and tar cuts obtained from tar fractionation. Secondly, a method to calculate vapor pressures of heavy hydrocarbons (and selected derivatives) as a function of temperature is sought. For this purpose, the SWAP method based on Prigogine's theory of large polysegmented molecules is being developed and applied to tar cuts obtained from tar fractionation.

In experimental work, vapor-pressure measurements of heavy aromatic hydrocarbons that are model compounds for coal-derived liquids are being made using a gas-saturation method for six heavy hydrocarbons and for five heavy nitrogen-containing hydrocarbons in the range 10^{-4} to 10^{-1} torr. Also, a technique is being developed to fractionate coal tars and to characterize the fractions (cuts). A spinning-band column is used for fractionation; typically 10 cuts are obtained with one measured vapor-pressure datum for each cut, which is subjected to elemental analysis and to ^{1}H-NMR measurements to obtain its aromaticity. Fractionation and characterization have been carried out for two tars, one from the Synthane process and the other from Research Triangle Institute (North Carolina). Finally, a computer program, suitable for heat-exchanger design, has been established for calculating isobaric dew-point temperatures for hot tar-containing gases.

PLANS FOR THE COMING YEAR — In the coming year, we plan to obtain additional vapor-pressure data, to fractionate and characterize additional tars, and to measure dew points in a flow apparatus, using actual tars. The dew-point apparatus has been built and is nearly ready for use.

WEAR-RESISTANT ALLOYS FOR COAL-HANDLING EQUIPMENT

UNIVERSITY OF CALIFORNIA, BERKELEY
DOE - $759,769
10/1/77 - 9/30/80
Principal Investigators - V.F. Zackay, E.R. Parker

OBJECTIVES — The objective of the program is to develop wear- and abrasion-resistant alloys for coal transportation and fragmentation equipment. It has been anticipated that large tonnages of coal will be mined, sized, transported, and handled because of the move towards utilizing coal as a major fossil fuel energy source. This increase in utilization will lead to severe wear problems in equipment components coming in contact with the coal because it contains abrasive particles that are generally much harder than the materials used in coal-handling equipment. Thus, there is a need to develop better abrasion-resistant alloys. The successful completion of this project will result in alloys with improved wear performance in specific coal-handling equipment, which would eventually improve the economics of using coal as an energy source.

RECENT WORK AND ACCOMPLISHMENTS — A new abrasive wear tester capable of simulating both two- and three-body wear in the laboratory was designed and constructed. This tester was used to determine abrasive wear factors of several experimental alloy compositions heat-treated to achieve various microstructures and mechanical properties. Two types of steels were developed: low-alloy ultra-high-strength and medium-alloy secondary hardening steels. Various compositions in both categories were investigated, and alloys possessing good combinations of strength and toughness were developed. The microstructure and mechanical properties of these steels were characterized. From a preliminary study of their wear behavior, it was possible to demonstrate the important role of microstructure on the measured wear rates, and the beneficial effects of microstructural features such as retained austenite, secondary carbides, and undissolved primary carbides. However, no clear correlation between mechanical properties such as hardness and toughness and abrasive wear was apparent. Specific applications in which the various developed steels may be used are as indicated; for example, for structural applications requiring a combination of strength, toughness, and abrasive wear resistance at elevated temperatures, steels of the secondary hardening type with a limited size and volume fraction of undissolved carbides would be optimal.

PLANS FOR THE COMING YEAR — The abrasive wear behavior of the developmental alloys will be determined under several different wear situations, such as high-stress three-body wear and impact wear. Most of the studies had been restricted to forged alloys. In the coming year, the mechanical properties and wear behavior of similar cast alloys will be determined. Attempts will be made to test some of the alloys in component form to determine the feasibility of using newly developed alloy compositions in specific coal-handling applications.

LOW-ALLOY STEELS FOR THICK-WALL PRESSURE VESSELS

UNIVERSITY OF CALIFORNIA, BERKELEY
DOE - $153,510
10/1/77 - 9/30/79
Principal Investigators - E.R. Parker, V.F. Zackay

OBJECTIVES — The objective is to adapt or develop low-alloy steels that can be fabricated into large-diameter thick-wall pressure vessels for coal gasification-liquefaction systems. The work centers around developmental studies on commercially available steels and on new alloy steel systems to meet this goal. The steels will have adequate strength and toughness in thick sections to assure reliable operation of large reaction vessels and microstructures aimed at improved environmental resistance. The steels will have sufficient fabrication "forgiveness" to allow on-site construction of containment vessels requiring limited post-weld heat treatments. Successful completion of the alloy development program will produce better steels for thick-section pressure vessels.

RECENT WORK AND ACCOMPLISHMENTS — Research on thick-plate simulations for fracture property characterizations centered around establishing the importance of specimen size and geometry in J-integral fracture tests. A limited amount of heat transfer analysis of thermal profiles in the heat affected zone (HAZ) of welded thick plates was also done. In the evaluation of commercial materials, 12-in. plate simulations of commercial A533B and A542 steels were done to increase baseline data. Detailed microstructural characterization was initiated to correlate structure-property relationships. Thick plate simulations were also carried out on commercial heats of modified Mn-Mo-Ni and Cr-Mo alloys. It was found that small amounts of Cr, Mn to A533B (Mn-Mo-Ni) and Ni, Mn to A542 (Cr-Mo) led to improved strength and toughness in 8-in. and 12-in. plates. Reversible temper embrittlement studies were carried out on commercial A543 (Ni-Cr-Mo) steels. It was found that minor additions of B and N were not helpful in reducing the temper embrittlement susceptibility. Considerable progress was achieved in the design of new alloys for thick-section pressure vessels. A broad understanding of the decomposition kinetics was achieved in the Fe-0.2C-1V system; with controlled heat treatments, fine dispersions of alloy carbides in a ferritic matrix gave optimum mechanical properties.

PLANS FOR THE COMING YEAR – Further fracture property characterizations are planned in order to establish useful fracture toughness tests for thick sections. Mechanical property characterization and microstructural evaluations of the commercial steels and their modifications will be completed. Some reversible temper embrittlement studies of the most promising alloys are also planned. Efforts are being aimed at optimizing the morphology of eutectoid mixtures formed during continuous cooling in order to investigate whether this class of steels can be used for thick-section pressure vessels.

OXYGEN STOICHIOMETRY AND ANALYSIS AND NITROGEN DETERMINATION IN COAL

UNIVERSITY OF CALIFORNIA, IRVINE
DOE - $138,660; UC, Irvine - $9600
3/1/76 - 6/1/79
Principal Investigator - G.E. Miller

OBJECTIVES – The objective is to examine fully the contribution neutron activation techniques can make to elemental analysis of fossil fuel materials with particular emphasis on precise determination of oxygen and nitrogen. Successful development and proof of additional multi-element capability would lead to recommendations for adoption of routine methods to supplement those used for fossil fuel characterization studies.

RECENT WORK AND ACCOMPLISHMENTS – Difficulties were encountered in sample provision and in technical operation of aging equipment. Replacement of major equipment is now underway, and full operation is resuming. Data already accumulated show that excellent precision is achieved for oxygen in all materials. The total nitrogen content of coal and related materials can be successfully measured by fast neutron activation methods and the precision attainable is comparable to that by traditional Kjeldahl methods except in cases where a large mineral content perturbs the nuclear analysis. Because only one sample can be run at a time, in comparison to dedicated Kjeldahl laboratory, the daily throughput will be much lower for the nuclear method. This disadvantage is offset by the fact that only a single sample preparation sequence is needed for the nuclear analysis for oxygen, nitrogen, and silicon. Silicon content data are obtained simultaneously with nitrogen data. These numbers also appear to be in excellent agreement with those obtained by traditional methods. In this case, the nuclear method is definitely simpler and probably more accurate than traditional methods.

PLANS FOR THE COMING YEAR – Data obtained are to be processed through simple computer plotting and correlation programs to examine fully the interrelationships in terms of assessed properties. Particular attention will be given to comparing these results with those used by others (especially the Pennsylvania State University group) to see if discrepancies arise or are eliminated by new data. The multi-element capability will be established by careful estimates of the precision attainable for other elements during "routine" determinations for O, N, and Si. Additional attention will be given to unusual samples where good agreement does not exist between these results and existing data.

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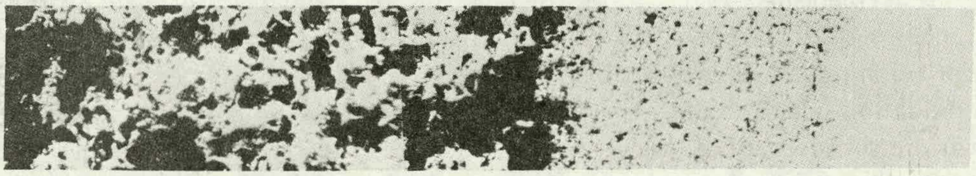
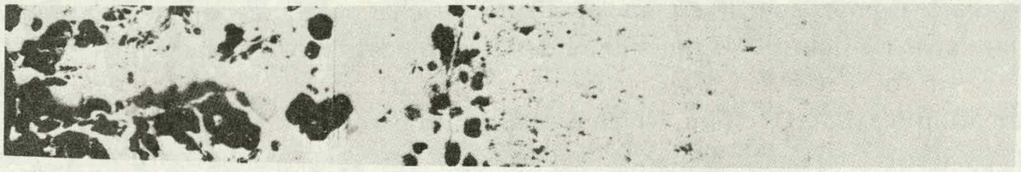
CORROSION OF STRUCTURAL MATERIALS IN CONTACT WITH COAL CHARS

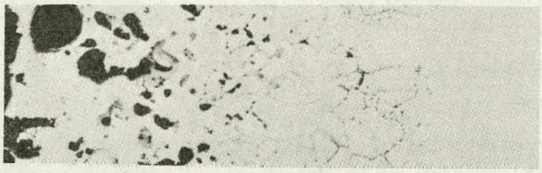
UNIVERSITY OF CALIFORNIA, LOS ANGELES
DOE - $123,574; UCLA - $11,519
3/1/77 - 2/28/80
Principal Investigator - D.L. Douglass

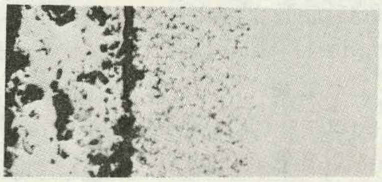
OBJECTIVES – The objectives are to measure the reaction rates between low- and high-sulfur coal chars and six alloys over the range of 1600° to 1800°F, to determine the mechanism(s) of reaction and the principal mode by which metal degradation occurs, and to determine the effect of preoxidation treatments on the behavior of the alloys in contact with coal chars.


Inconel 671


310 Stainless


Hastelloy X


Incoloy 800


Haynes 188

RECENT WORK AND ACCOMPLISHMENTS – Six alloys–310 stainless steel, Hastelloy X, Inconel 671, Incoloy 800, Haynes 188, and FeCrAℓY–have been exposed to two chars at 1600° and 1800°F for up to 96 hr. The chars, FMC and Husky, contain 2.7 and 0.9 percent S, respectively. Various parameters have been studied, including char size, cover gas, char quantity, char replenishment period, and gas-flow rates. Corrosion kinetics have been determined by weight gain measurements when feasible (if spalling of the scales and sticking of char to the scales do not occur extensively). Metal recession rates and the rate of thickening of the internal reaction-product zone have been measured by metallographic techniques. Identification and characterization of the reaction products have been performed by X-ray diffraction, dispersive X-ray energy analysis, metallography, and electron microprobe analysis. Gas analyses have been made by wet chemical methods and gas chromatography. Corrosion by char is much more severe than by gas (CGA) in a coal gasifier. Char corrosion causes massive sulfidation compared to oxidation and sulfidation by CGA. Char corrosion formed thick nonprotective sulfide scales (generally iron and nickel sulfides) and a zone of internal attack consisting of the more stable sulfides such as Cr_3S_4. No carburization has been observed. The corrosion kinetics were nearly linear with time. For samples exposed at 1800°F in high-sulfur char replenished every 12 hr, the rates were strongly influenced by the char-replenishment frequency resulting from sulfur depletion of the char. The more often new char is used, the higher the corrosion rate. A char-quantity effect was observed that is related to the H_2S content of the gas. No oxidation occurred until the sulfur in the char was depleted; then, the gas composition shifted from the sulfide-stability region to the oxide stability region in the respective thermodynamic stability diagrams. The most corrosion-resistant alloy in CGA, Inconel 671, was the worst in high-sulfur chars. Comparison of extrapolated rates in char to those obtained in CGA shows that corrosion in char is about 3000 times more rapid. Preoxidation had no beneficial effect on char corrosion except for FeCrAℓY, which showed a marked improvement. The effect is attributed to the formation of an $Aℓ_2O_3$ film, which prevents sulfur from contacting the substrate.

PLANS FOR THE COMING YEAR – Long-term tests (500 to 1000 hr) will be run. Reaction mechanisms will be determined. The role of preoxidation will be completely evaluated.

ANALYSIS OF HYDROGEN ATTACK ON PRESSURE VESSEL STEELS

UNIVERSITY OF CALIFORNIA, SANTA BARBARA
DOE - $308,589
7/13/78 - 7/13/81
Principal Investigator - G.R. Odette

OBJECTIVES - Future energy sources involving the hydrogenation of coal will impose severe demands on the materials used to contain the processes. Current engineering control of hydrogen damage is based on the Nelson curve, which is a set of empirical hydrogen partial pressure-operating temperature curves developed in the petrochemical industry to avoid failure. The objectives of this program will be to develop statistically based Nelson curves using the latest data and current theoretical models for hydrogen attack to interpolate and extrapolate about the experimental data, and identify tests and theoretical concepts whose future development will provide for improved control of hydrogen attack.

RECENT WORK AND ACCOMPLISHMENTS – Available literature is being used to develop a computerized data base of hydrogen attack observations and to guide development of hydrogen attack models. Initial model development has concentrated on surface decarburization.

PLANS FOR THE COMING YEAR – Data used to generate the original Nelson curve will be gathered, qualified, and entered into a computerized data base. Additional data related to hydrogen attack will also be amassed, such as laboratory research data, kinetic and thermodynamic data, and engineering data from related processes (such as boiler damage). Work on the surface decarburization model will continue with the goal to match the model predictions with plant experience. Model development will then be extended to the simulation of internal bubble and fissure formation. Efforts will be made to establish the relationship between hydrogen damage microstructure and degradation in mechanical properties. The development of flaw and fracture maps for hydrogen damage will be initiated.

CHEMISTRY AND STRUCTURE OF COAL-DERIVED ASPHALTENES

UNIVERSITY OF SOUTHERN CALIFORNIA
DOE - $30,600; USC - $12,200
7/1/75 - 12/19/78
Principal Investigator - T.F. Yen

OBJECTIVES — This project is investigating the nature of asphaltene to elucidate its role in coal liquids. Understanding the chemistry and structure of coal-derived asphaltene is essential to the development of an efficient coal liquefaction process. Asphaltene affects the quantity and quality of oil produced. Knowledge regarding the generation of asphaltene will help to eliminate coke formation. Heterocyclic atoms (sulfur, nitrogen, oxygen) as well as metals and ashes tend to concentrate in the asphaltene fraction. Asphaltene and its high molecular weight derivatives (carbene and carboid) are responsible for high viscosity, solvent imcompatibility, and processing instabilities. It is anticipated that correlation of structural parameters with conversion and refining variables will yield useful information for the design and operation of an efficient coal liquefaction process.

RECENT WORK AND ACCOMPLISHMENTS — An X-ray diffraction method has been developed for characterizing the macrostructure of solid coal liquid products, including a number of structural parameters. Information obtained from the use of ^{1}H- and ^{13}C-NMR techniques, elemental analysis, VPO molecular weight, and chemical functionality data has been correlated to obtain the average structure of asphaltene. Other physical data such as thermogravimetric analysis, gel permeation chromatography, statistical densimetric method, and polarographic analysis support the hypothetical structure. Chemical methods such as silylation, methylation, and oxidative degradation studies also support the physical methods employed. Comparison of the structure of asphaltene, resin, and carbene or carboid has been tentatively derived.

PLANS FOR THE COMING YEAR — Characterization of the benzene-insoluble fraction will be the major objective for the coming year. Using the available methods derived for the benzene-soluble fractions, data will be obtained for the benzene-insoluble fractions of coal liquids (i.e., pre-asphaltenes or post-asphaltenes such as carbene and carboids).

APPLICATION OF DIELS-ALDER REACTION TO COAL FRACTIONATION

UNIVERSITY OF SOUTHERN CALIFORNIA
DOE - $40,000
8/1/77 - 7/31/79
Principal Investigator - T.F. Yen

OBJECTIVES — The technical objectives of this project are twofold: first, to obtain information on the structure of the different coal components in order to provide valuable insights into the process of taking them apart; and second, to examine the feasibility of applying the Diels-Alder reaction to fractionating coal into useful raw materials. The practical advantages of this work will be: comminution or size reduction of coal; separation of pyrite or other minerals; and fractionation of coal (at least the olefins).

RECENT WORK AND ACCOMPLISHMENTS – Native coal samples from Penn State representing low-volatile bituminous and high-volatile bituminous coals and lignite were extracted exhaustively with solvent to isolate coal components such as asphaltene and resin. Various physical methods were used to characterize the native coal asphaltenes. Lignite-derived asphaltene has lower aromaticity than that of others. The reactions of coal with dienophiles—sulfur dioxide and acrylonitrile—have been studied preliminarily. In the case of sulfur dioxide, coal samples with different ranks were allowed to react in a vessel at temperature of 76°C and pressure of 200 psi. A very small amount of yellow oily liquid was produced and the surface of coal appeared to be friable after reaction. The weight loss of the coal samples (range from 2 to 8 percent) indicates that lignite is more reactive towards sulfur dioxide than low-volatile bituminous coal. A high-pressure reaction system equipped with Magnedrive stirring, as well as sample injection loading and withdrawal, has been constructed. A number of dienes and dienophiles with appropriate solubility parameters and hydrogen conding capacities have been selected.

PLANS FOR THE COMING YEAR – Studies will be made of high-temperature and pressure reactions of different ranks of coals with dienophiles (such as paraldehyde, nitrobenzene) and with dienes (such as chloroprene, hexachlorocyclopentadiene) in an autoclave. Different polymerization inhibitors will be tested.

CLEAN SOLID AND LIQUID FUELS FROM COAL

COLORADO SCHOOL OF MINES
DOE - $656,417; CSM - $73,440
10/1/75 - 4/7/79
Principal Investigators - J.H. Gary, J.O. Golden

OBJECTIVES – This research has the goal of producing an environmentally acceptable fuel from coal. This fuel may be either solid or liquid, depending upon processing conditions and operational mode chosen. Environmental Protection Agency Ambient Air Quality standards are being used as guidelines for fuel quality. An ash-containing, low-sulfur, low-nitrogen fuel that may be burned in new and existing power-generating facilities is the primary objective. A secondary objective is the production of a suitable refinery feedstock.

RECENT WORK AND ACCOMPLISHMENTS – Studies have been completed to develop global rate models for the removal of sulfur from coal and for the conversion of coal to preasphaltenes, asphaltenes, and oils. These investigations were carried out using quick-charge batch reactors. Research is in progress to determine the effect of continuous processing parameters upon sulfur removal kinetics and coal conversion using the specially developed bench-scale unit. Included in these parameters are temperature, pressure, residence time, and reactor configuration. The effects of inexpensive catalysts upon the generation of in situ hydrogen from CO-steam and upon coal conversion have been studied in batch experiments. A promising catalyst has been found and a conversion rate model developed. The removal of nitrogen from an SRC process-derived solvent is being studied to identify promising commercial catalysts for hydrodenitrogenation (HDN). Various reactor systems are being used to make the catalyst evaluations, with the present one being a continuous trickle bed reactor. Kinetic models are being developed to predict the removal rates for specific nitrogen compounds (such as carbazole, tetrahydroquinoline, and quinoline) during catalytic HDN processing operations. Work is continuing on the separation and classification of compounds in coal-derived materials. Recent emphasis has been placed upon analysis of nitrogen fractions.

PLANS FOR THE COMING YEAR — Extensive coal conversion data will be obtained using the continuous bench-scale unit. Further investigations will be performed of low-cost catalysts and of the kinetics of HDN using pseudo-model compounds generated from the nitrogen-rich fraction of a coal-derived oil.

ENTHALPY MEASUREMENT OF COAL-DERIVED LIQUIDS

COLORADO SCHOOL OF MINES
DOE - $277,683; CSM - $30,854
6/24/75 - 3/31/79
Principal Investigators - A.J. Kidnay, V.F. Yesavage

OBJECTIVES — Thermodynamic property research is recognized as invaluable by process and design engineers in the petroleum, chemical, and allied industries. Calorimetric measurements of specific heats or enthalpies, pressure-density-temperature measurements, and phase equilibrium determinations for pure fluids or complex mixtures are all essential for the optimum design of both physical and chemical processing units. Coal-derived liquids are a new and vital class of industrial compounds but have thermodynamic properties that are largely unknown and, presently, unpredictable. The objective of this research is to measure one of the most important thermodynamic properties—enthalpy—for representative coal-derived liquids over the pressure and temperature regions most likely to be encountered in both liquefaction and processing systems. The research is divided into three major program areas: design, construction, and evaluation of freon boil-off calorimeter for temperatures to 800°F and pressures to 2000 psig; enthalpy measurements on approximately 10 samples of coal-derived liquids; and preparation of engineering correlations for the measured enthalpy data, and comparison with representative data for petroleum and petroleum fractions.

RECENT WORK AND ACCOMPLISHMENTS — Enthalpy measurements were completed on three samples of coal liquids. To date, 563 enthalpy measurements have been made on eight samples of coal liquids in the ranges 65° to 750°F and 30 to 1500 psia. In conjunction with Texas A&M University, an analytical program was initiated to characterize the coal liquid samples. Work on this program is continuing.

PLANS FOR THE COMING YEAR — Work will begin on the enthalpy measurements for model compounds, such as benzene, m-xylene, and l-methylnaphthalene; and work will continue on the analysis and characterization of the coal liquids.

ELECTROSLAG WELDING PROCEDURES

COLORADO SCHOOL OF MINES
DOE - \$233,765; CSM - \$12,303
6/30/78 - 6/29/81
Principal Investigator - G.R. Edwards

OBJECTIVES – The cost-effective joining of thick-section pressure vessel steels is crucial to the advancement of fossil energy technology. Current designs for coal liquefaction and gasification vessels require high-quality weldments of steel ranging up to 14 in. in thickness. One of the most cost-effective joining processes for heavy sections is electroslag welding; however, the scarcity of data in the open literature concerning the electroslag welding metallurgy of pressure vessel steels has slowed its acceptance by industry. The objective of this research is first to investigate the microstructural and mechanical integrity of 2¼ Cr - 1 Mo steel electroslag weldments fabricated by commercial practice techniques, then to apply concepts of process control and flux refinement to accomplish the improvement of weldment properties.

RECENT WORK AND ACCOMPLISHMENTS – Much of the initial effort has been to microstructurally characterize commercial-quality weldments of 4-in.-thick A 335 steel, then to correlate weldment microstructures both with the thermal history during welding and with the mechanical integrity. Microstructures observed correlate well with predictions, a fine bainitic fusion zone and a heat-affected zone of acicular ferrite have been observed. Tensile samples machined to include the fusion zone, the heat-affected zone, and the metal within the gage length have failed by ductile fracture of the base metal. Cyclic fatigue testing of such samples also resulted in failure of the base metal. Fatigue crack initiation occurred at approximately 1.5×10^6 cycles of a tension-tension (4500 psi to 45,000 psi) test. Charpy impact specimens notched at ¼-in. intervals across the entire weldment cross section are being tested to help isolate the minimum-toughness zone of the initial specimens. A study of the welding parameters for the electroslag process has shown that the achievement of sufficient fusion is relatively sensitive to the heat input per vertical inch of weldment. A constitutive equation, dependent on welding current, voltage, and root spacing, has been developed to express the critical value of heat input per inch necessary for sufficient penetration. This relation is based on empirical observations of the minimum heat input required to prevent lack of fusion in the first generation weldments.

PLANS FOR THE COMING YEAR – The constitutive equation to quantify satisfactory limits for the welding parameters of voltage, amperage, and root spacing will be refined by experiment. Two different slag experiments are being prepared based on baked Hobart PF-201 electroslag welding flux, a typical commercial product. One experiment will evaluate the effect of small oxide additions to the commercial flux on the ultimate weld quality. The second experiment will determine the influence of flux moisture on final weld integrity. Appropriate specimens are being extracted from flux material before and after welding, from parent metal, and from the weld metal for chemical analysis. Test procedures duplicating the metallographic and mechanical analyses completed on as-welded specimens will be performed on weldments stress-relieved by standard ANSI B 31.1 procedures. An evaluation of how standard stress-relief procedures affect the microstructure and mechanical behavior of weldments will result from the comparison.

NEW PROCESS FOR PRODUCING CARBON MONOXIDE AND HYDROGEN

COLORADO SCHOOL OF MINES
DOE - \$40,000; CSM - \$7,188
9/77 - 9/79
Principal Investigator - E.D. Sloan

OBJECTIVES — The objective is to provide basic kinetic data on the reaction $P_4O_{10} + 10\ C \rightarrow 10CO + P_4$ as a second reaction in a coal gasification process. A secondary objective is to consider P_4O_{10} solid phase transitions. The combination of the first reaction with a second better known reaction $P_4 + 10H_2O \rightarrow P_4O_{10} + H_2$ yields two combustible gases from C and H_2O. Basic kinetic data on the initial reaction will lead to pilot plant studies.

RECENT WORK AND ACCOMPLISHMENTS — The method for analysis of the phosphorus oxides compounds has been validated. A chromatograph has been constructed for the analysis of CO and CO_2; it is being calibrated. Construction of the experimental equipment will be completed by May 1, 1979. Safety requires a hood with independent ventilation, in addition to the reactor and auxiliary equipment.

PLANS FOR THE COMING YEAR — Initial kinetic data will be taken in a tubular reactor and analysis will be performed.

SIMULATED NON-EQUILIBRIUM ENERGY DISTRIBUTIONS IN STEAM/COAL CHAR REACTION

UNIVERSITY OF COLORADO
DOE - \$47,346; Colorado U - \$1819
3/1/76 - 8/31/79
Principal Investigator - L.F. Brown

OBJECTIVES — The objective of this work is to determine the potential feasibility of inducing non-equilibrium molecular energy distributions in a reacting steam/coal char system. The purpose is to allow the reaction to be run at a substantially reduced temperature compared with present systems.

RECENT WORK AND ACCOMPLISHMENTS — The project has been divided into four phases. *Determination of probable paths of reaction*: Earlier literature studies and associated calculations indicated that the rate-limiting step in the steam/coal char reaction is the desorption of carbon monoxide from the graphitic crystallite in the char. This step apparently is complicated by the presence of surface diffusion of the carbon monoxide prior to desorption. Further literature study has reinforced these conclusions. *Study of solid-phase excitation*: Since the desorption of the product carbon monoxide is what limits the rate of this reaction, stimulating this desorption must be the primary goal of any technique involving non-equilibrium energy distributions. Stimulation of this desorption implies exciting the bond that holds the carbon monoxide to the surface, here described as "solid-phase excitation." The bond to be broken may be the carbon-carbon bond where the carbon monoxide is attached to the graphitic surface, or it may be whatever bond holds a diffusing mobile carbon monoxide molecule to the carbonaceous surface. Study of this step involved investigations of the literature concerning the desorption of carbon monoxide from carbon surfaces; the use of infrared spectroscopy to study adsorption on carbon surfaces, particularly the adsorption of carbon monoxide, oxygen, and oxygen compounds; and the excitation of homogeneous reactions stimulated by laser radiation for applicability to this problem. Available lasers were studied for their use in stimulating desorption, and it was concluded that such experimental studies are possible and desirable. *Study of gas-phase excitation*: It was calculated that the excitation of the gas phase would be desirable only at certain very high levels of the solid-phase excitation, which requires experimental evidence of the ability of the available techniques to provide sufficient excitation of the solid phase. *Development of experimental program*: Further study was made of experimental techniques for investigating the possibilities of creating the desired non-equilibrium energy distributions in the reacting species of the steam/coal char reaction.

PLANS FOR THE COMING YEAR — The literature concerning determination of probable paths of reaction will be monitored, and some further calculations may be carried out. In solid-phase excitation studies, a possible serious problem remains in that excitation of the bond involved may relax before any reaction might take place. This possibility will be studied further. Studies of gas-phase excitation are essentially complete, with only the final report writeup remaining. Experimental program development will receive major emphasis since overcoming design problems will require much effort.

ELEVATED TEMPERATURE EFFECT ON CREEP BEHAVIOR OF OIL SHALE

UNIVERSITY OF COLORADO, DENVER
DOE - $49,670; UCD - $19,856
9/1/78 - 8/31/80
Principal Investigator - N.Y. Chang

OBJECTIVES — Creep behavior of oil shale is strongly dependent on stress, temperature, and its organic (kerogen or oil) content. This functional relationship is termed "creep function," and its key parameters will be functions of organic content of oil shale. This study is designed to formulate a proper creep function. Creep tests will be conducted on oil shale specimens of different kerogen richness and under different combinations of stresses and temperatures, with emphasis on the uniaxial creep of oil shale under elevated temperatures.

RECENT WORK AND ACCOMPLISHMENTS — Effort has been concentrated on the procurement of laboratory testing equipment: five Conbel Model 357 Units (from Karol Warner, Inc., of Highland Park, N.J.) and a deformation transducer. Uniaxial and triaxial test cells are being designed. Since both strength and Young's modulus of oil shale are strongly dependent on temperature, tests are being conducted to establish strength versus temperature and Young's modulus versus temperature relationships. Oil shale specimens of different grades are being used in these tests.

PLANS FOR THE COMING YEAR — Work to be accomplished includes: design of a laboratory testing system with uniaxial test cells for creep tests under elevated temperature; high-temperature property and strength tests for five different grades of oil shale; high-temperature uniaxial creep tests for two grades of oil shale; formulation of a functional relation of the uniaxial strength and the Young's modulus versus temperature and uniaxial creep functions for the results from the second and third items of work; and designing a high-temperature triaxial test system.

DEVELOPMENT OF SULFUR-TOLERANT CATALYSTS

UNIVERSITY OF COLORADO (U)
DOE - \$40,000; Colorado U - \$5100
9/1/77 - 8/31/79
Principal Investigator - M.C. Rakowski

OBJECTIVES — The catalytic properties of polynuclear molybdenum complexes with sulfur ligands are being investigated to develop a sulfur-tolerant catalyst system for the reduction of carbon monoxide. Such sulfur-tolerant catalysts would find application in the conversion of coal to high-Btu gaseous fuels with a minimum of synthesis gas processing. In particular, they are important in single-stage reactors that do not include a mechanism for coal gas desulfurization prior to methanation.

RECENT WORK AND ACCOMPLISHMENTS — A dimeric molybdenum compound with sulfur ligands, $[C_5H_5MoSC_nH_{2n}S]_2$, where n = 2 or 3, has been found to function under mild homogeneous conditions as a sulfur-tolerant catalyst in the hydrogenation of certain unsaturated hydrocarbons. Two steps in the catalytic cycle have been characterized. The molybdenum complexes, which contain bridging 1,2 ethane- or 1,2 propanedithiolate ligands, undergo a remarkable reaction with alkenes and alkynes in which the hydrocarbon portion of the bridging dithiolate ligands is exchanged (e.g., Reaction 1). The production of ethene

$$C_5H_5Mo\,(S\quad S)_2MoC_5H_5 + \underset{(1\ \mathrm{atm})}{C{\equiv}C} \quad \overset{25^{o}}{\underset{CHC1_3}{}} \quad C_5H_5Mo\,(S\quad S)_2MoC_5H_5 + C=C \quad (1)$$

in Reaction 1 has been confirmed by gas chromatographic studies, and the product complex with 1,2 ethenedithiolate bridges has been characterized by several spectral techniques. Analogous reactions of the complexes with alkenes have also been characterized. The product of Reaction 1 can be hydrogenated under mild conditions (Reaction 2), and this constitutes

$$C_5H_5Mo\,(S\quad S)_2MoC_5H_5 + \underset{(2\ \mathrm{atm})}{H_2} \quad \overset{65^{o}}{\underset{CHC1_3}{}} \quad C_5H_5Mo\,(S\quad S)_2MoC_5H_5 \quad (2)$$

the second characterized step of the cycle (Reactions 1 and 2), which catalyzes the hydrogenation of acetylene to ethylene. No further reduction occurs under these conditions. The hydrogenation cycle is unaffected by hydrogen sulfide (present at levels of 4 to 5 percent by volume). The sulfur-tolerant catalyst system is fundamentally different from other catalysts composed of transition metal complexes in that the sulfur ligands play an active role in the catalytic cycle. A possible intermediate in the alkyne exchange reaction, $[C_5H_5MoS_2]_2$, has been prepared by a separate route and found to react in an analogous manner with acetylene and hydrogen to form ethylene.

PLANS FOR THE COMING YEAR — The ability of the molybdenum complexes to function as catalysts for the hydrogenation of carbon monoxide will be investigated. Studies will include product analysis of the reaction of the metal complex with CO and H_2 at varied pressures, as well as attempts to characterize intermediate complexes that may be formed during a catalytic cycle. Attempts will be made to modify the catalyst by changing oxidation state or ligand substituents in order to determine optimum conditions for catalytic activity.

IN SITU NONCOMBUSTION MICROWAVE PROCESSING OF OIL SHALE

UNIVERSITY OF COLORADO, DENVER
DOE - $38,843
9/78 - 4/79
Principal Investigator - E.T. Wall

OBJECTIVES – The development of a microwave-heated in situ method of extracting the hydrocarbon fractions from kerogen is the goal of this program. While current methods rely on combustive heating, it is important that other methods be investigated. Microwave retorting, a closed noncombustion system, eliminates much of the pollution of present systems; allowing the use of retorting gases, otherwise lost by dilution, thus maximizing resource recovery; and appears to be a more rapid method of retorting. This program phase involves a total elemental analysis of the microwave-produced oil and gas fractions, using a microcoulometric approach. These data will be compared with results obtained by chromatography.

RECENT WORK AND ACCOMPLISHMENTS – A comprehensive mechanism for gas formation from shale and other solid fuel sources is being formulated with comparative gross gas analysis. More rapid sulfur analysis in the liquid produced has yielded results comparable to the general theory of localized microwave interactions. Increased laboratory shale oil generation has permitted macro analysis of the shale oil properties to be started for comparison with other process products. Instrumentation has been procured and set up that will allow full-scale experimentation to begin soon. An important development has been the completion and testing of a secondary cavity for installation in the 1300-watt microwave multimode unit, which permits processing of up to 5-kg of shale or other fuel precursors. The stainless steel construction permits greater flexibility in gas pressure ranging to study changes in product kinetics.

PLANS FOR THE COMING YEAR – The microwave dielectric measurement equipment will be extended to give direct readout of input and output electrical power requirements for a given sample of fossil fuel, which will give better control in the energy balance tests for given samples. The data obtained will be used in the design of microwave applications and power units to be used in large-scale prototype tests.

ELECTROCHEMICAL GASIFICATION OF COAL

UNIVERSITY OF CONNECTICUT
DOE - $40,000; Connecticut U - $32,000
9/1/77 - 8/31/79
Principal Investigator - R.W. Coughlin

OBJECTIVES – A preliminary experimental investigation is being conducted of gasification of coal by its anodic oxidation in an electrochemical cell. By this method, the carbon in coal is converted to oxides of carbon and the hydrogen in coal is converted to hydronium ions at the anode.

RECENT WORK AND ACCOMPLISHMENTS – The electrochemical gasification of coal has been successfully demonstrated with several different fuels: Pittsburgh Seam Coal, Illinois No. 6 Coal, Montana Rosebud Coal, Montana Rosebud Char, North Dakota Lignite; also coke, carbon blacks, and graphite have been gasified by this new process. The experiments were carried out at room temperature and temperatures up to about 110°C, at 1 atm pressure. The electrolyte was

20 percent sulfuric acid, and the electrodes were of platinum with a porous glass frit separating the anode and cathode compartments of the cell. The solid fuel was in pulverized form (100 to 200 μm particle size), and it was suspended in the anolyte. Gasification took place at overall cell potentials as low as 0.8 volt, and pure hydrogen was produced at the cathode. The gas produced at the anode was mostly CO_2, with some CO (3 to 7 percent). There was no evidence of pollutants such as SO_2 in either of the gaseous products even when the fuels gasified by this method contained significant quantities of sulfur. Some other nongaseous products were also produced: carbon-containing compounds that dissolved in the aqueous electrolyte and tar-like substances that could be extracted by organic solvents from the partially reacted solid fuel. Some preliminary experiments have also been conducted to investigate variables such as temperature, cell potential, concentration of solid fuel in electrolyte, nature and concentration of electrolyte, particle size of solid fuel, type of electrodes, and areas of electrodes.

PLANS FOR THE COMING YEAR – Experiments will continue in an effort to gain a better understanding of the process and the products produced. Chemical analysis and quantitative collection of all products should permit material balances to be made. In addition, various types of electrolytes and electrodes will be tested and further investigated if the results suggest improvement. Attempts will also be made to operate the process over a wider range of temperatures. Energetic and thermodynamic efficiencies of the process as well as economic projections will also be considered.

KINETICS AND MECHANISM OF DESULFURIZATION/DENITROGENATION OF COAL-DERIVED LIQUIDS

UNIVERSITY OF DELAWARE
DOE - \$726,000; Delaware U - \$238,000
6/20/75 - 1/31/79
Principal Investigators - B.C. Gates, J.R. Katzer

OBJECTIVES – The goals of this project are to determine reaction networks and reaction kinetics for catalytic hydrodesulfurization and hydrodenitrogenation of compounds found in coal-derived liquids; relative reactivities of sulfur- and nitrogen-containing compounds in coal-derived liquids and structure-reactivity patterns; quantitative data characterizing the chemical and physical properties of catalysts aged in coal-liquefaction processes; mechanisms of deactivation; and reaction engineering information and models to predict the behavior of catalytic hydroprocessing of coal-derived liquids.

RECENT WORK AND ACCOMPLISHMENTS – Previously obtained data have been reevaluated, providing quantitative determination of the reaction networks and kinetics of catalytic hydrodesulfurization of dibenzothiophene, methyl-substituted dibenzothiophene, and benzo[b]naphtho[2,3-d]thiophene; and catalytic hydrodenitrogenation of quinolines, acridine, and carbazole. The catalysts were commercial hydroprocessing catalysts sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$, $NiO\text{-}MoO_3/\gamma\text{-}Al_2O_3$, and $NiO\text{-}WO_3/\gamma\text{-}Al_2O_3$. Under typical conditions of 300°C and 104 atm, dibenzothiophene reacted to give H_2S and biphenyl in high yield, but some hydrogenation accompanied hydrodesulfurization. The Ni- and W-containing catalysts give relatively more hydrogenation than the Co-containing catalyst, and the important result is that all three catalysts had approximately the same activity and all were highly selective for sulfur removal. Methyl-substituted dibenzothiophenes react similarly to dibenzothiophene; each reaction is pseudo first-order in the sulfur-containing compound. With methyl groups near the sulfur atom (in the 2 and 4 positions), the primary hydrogenation reaction is approximately as fast as the primary hydrodesulfurization reaction. Studies of the hydrodesulfurization of multi-ring sulfur-compounds (with Co-Mo/γ-Al_2O_3 at 300°C and 70 atm of H_2) show that the reactivity decreases from 1- to 3-ring compounds and then increases for the 4-ring compound. The 3-ring compound, dibenzothiophene, and its methyl-substituted derivatives are therefore the least reactive compounds studied. A three-point adsorption of thiophenic compounds has been suggested to be important in the surface-catalyzed hydrodesulfurization mechanism. This new mechanism accounts for the observed substituent effects and the effects of the number of rings in the reactant.

In contrast to sulfur-containing compounds, nitrogen-containing aromatics require hydrogenation of the aromatic ring before C-N bond rupture occurs. Saturation of the o-propyl aniline is required before nitrogen removal; propylcyclohexane is the primary hydrocarbon product. The reaction network for carbazole is similar. Acridine and its homologs appear to be among the least reactive nitrogen-containing compounds in coal-derived liquids. Studies of competing hydroprocessing reactions catalyzed by NiMo/γ-Al_2O_3 and involving quinoline, indole, dibenzothiophene and naphthalene show that marked interactions exist. Aged catalysts taken from the Synthoil and H-Coal^R processes and a proprietary fixed-bed process were analyzed with an electron microscope, with an electron microprobe, and by energy dispersive X-ray analysis. Deactivation occurs by coking, by mineral-matter deposition in the interior and on the exterior of the catalyst, and by reductive deposition of iron and titanium in the interior of the catalyst. The scouring action of the ebullated bed of the H-Coal^R process prevents accumulation of mineral matter on the catalyst exterior; however, activity checks with aged catalyst from the H-Coal^R process before and after the burning off of carbonaceous deposits indicate that irreversibly deposited inorganic matter on the interior catalyst surface was responsible for much of the loss in activity.

PLANS FOR THE COMING YEAR — A new project will involve characterization of the hydroprocessing of fractions separated out of SRC II liquid.

NATIONAL COAL POLICY PROJECT

GEORGETOWN UNIVERSITY
DOE - $100,000; Other - $450,000
4/78 - 9/79
Principal Investigator - F.X. Murray

OBJECTIVES — The objective of the National Coal Policy Project is to bring together individuals from industry and environmental organizations in an effort to achieve agreement on policy recommendations concerning the increased utilization of coal within economically and environmentally acceptable limits. The project attempts to address the national inability to resolve the environmental objections to the burning of coal in a satisfactory manner. Five task forces composed of equal numbers of environmentalists and industrialists have been established by the Project to study coal-related issues in the areas of: Coal Mining, Coal Transportation, Air Pollution, Fuel Utilization and Conservation, and Energy Pricing. Discussions are conducted under the "Rule of Reason," whereby agreement is first sought on the relevant "facts" in order to make possible reasoned, unemotional consideration of the issues. The task forces are directed by the Plenary group, the Project's oversight body, composed of the Co-Chairmen and Vice Co-Chairmen of the task forces, and the Chairmen of the caucuses of each side.

RECENT WORK AND ACCOMPLISHMENTS – Phase I of the National Coal Policy Project was concluded in February 1978 with the publication of the report entitled *Where We Agree* (Westview Press, 1978). *Where We Agree* contains more than 200 consensus agreements and recommendations in the five task force areas. A companion summary and synthesis report was published in December 1978 (Center for Strategic and International Studies, Georgetown University, 1978). Following the release of *Where We Agree*, the Project's recommendations were presented to interested industrial, environmental, academic, and governmental representatives at more than 45 conferences, meetings, and seminars at various locations across the country.

PLANS FOR THE COMING YEAR – The Project's Plenary group met on December 19, 1978, in Washington to set an agenda for another working phase. Among topics to be addressed in this phase will be: Federal Coal Leasing Policy, Best Available Control Technology, Prevention of Significant Deterioration of Air Quality, Plant Siting in Non-Attainment Areas, Pricing of Cogenerated Electric Power, Synthetic Gas Pricing, and Social Impacts of Higher Energy Prices. The Project is expected to continue through the fall of 1979. A final report and interim reports will be issued.

INDUSTRIAL APPLICATION FLUIDIZED-BED COMBUSTION

GEORGETOWN UNIVERSITY
DOE - $9,871,061; Georgetown U - $4,611,962
6/76 - 5/82
Principal Investigator - B.A. Scarbrough

OBJECTIVES – The program includes the design, construction, testing, and operation of a 100,000 lb/hr fluidized-bed coal-fired saturated-steam (625 psig) demonstration boiler plant at Georgetown University, Washington, D.C. The plant will be fueled with low-quality high-sulfur content (3.5 to 4 percent) coal. It is intended to prove that this type of plant, in the capacity range of 15,000 to 150,000 lb/hr, is particularly adaptable to central heating-cooling plants for existing and future health and educational facilities. In addition to meeting air pollution standards, the plant will be designed to be: aesthetically and operationally acceptable in a university/medical complex environment, built and operated with time schedules and costs equal or better than conventional coal-fired plants, operated reliably and efficiently by personnel with experience typical of institutional boiler plants, and capable of operating efficiently over wide swings in load with and without oil/gas fired boilers in parallel.

RECENT WORK AND ACCOMPLISHMENTS – Design of the plant was completed in October 1977. Actual construction began the same month with a scheduled completion date of February 1979. Separate construction subcontracts were awarded for general construction, steel fabrication and erection, mechanical work, electrical work, and instrumentation. Coordination of the construction effort at the site is being performed by Pope, Evans and Robbins, Inc. Design, fabrication, and installation of the fluidized-bed boiler is being accomplished by Foster Wheeler Energy Corporation. As of October 1, 1978, construction was approximately 50 percent completed. Major items of prepurchased equipment were in place. Boiler erection was underway.

PLANS FOR THE COMING YEAR – Because of delays and design changes, the construction completion date has been extended to May 1979. Startup testing will begin immediately thereafter and last for a period of 3 months. The 33 month operation period is scheduled to begin in September 1979. Recruitment and training of personnel will be accomplished before startup.

SECOND LAW ANALYSIS WORKSHOP

THE GEORGE WASHINGTON UNIVERSITY
DOE - $97,460
9/78 - 8/79
Principal Investigator - A. Cambel

OBJECTIVES – This program involves planning and conducting a research workshop on the use and application of Second Law Thermodynamics Analysis of energy conversion processes. It is generally agreed that although the Second Law of Thermodynamics dates back to its first elucidation by Sadi Carnot in 1824, the Law has received little other than academic attention. Engineers tend to calculate thermodynamic efficiencies according to a simple calculation utilizing total energy supplied to a system and the resultant useful work. This has commonly been called "First Law Efficiency." It ignores the concept that there is a quality factor associated with energy in its various forms; for example, the energy in a gallon of high-test gas is of higher quality or has higher "availability" than an identical amount of energy bound up in room-temperature air. The Second Law satisfies this engineering deficiency by using the maximum amount of energy available in the energy medium supplied and the minimum amount of energy needed to accomplish the task assigned. The Second Law then measures the best that a system can perform according to the laws of physics. The objective, then, is to widen the knowledge and use of Second Law Analysis by providing fundamentals, tutorial applications, and novel applications contributed by the participants. Workshop discussion will provide common understanding of principles and approaches. The publication of a Proceedings will complete the objective, as it will serve to provide a single repository of standard engineering knowledge and approaches to applications for the use of all engineers.

RECENT WORK AND ACCOMPLISHMENTS – An announcement and call for papers was drafted, printed, and distributed to over 14,000 engineers of diverse disciplines and organizations. Approximately 300 responses have been received plus over 50 abstracts for contributed papers. Commitment has been obtained from approximately 15 authors of invited papers, and a planning program is in the final draft stage. The Ballroom of the Marvin Center at The George Washington University has been obtained for the Workshop and the dates set for August 14 to 16, 1979. An Executive Committee, chosen from the most eminent thermodynamic authorities, has guided this work.

PLANS FOR THE COMING YEAR – The program will be finalized. A major effort will be mounted to achieve the best possible participation. The Workshop will be held and Proceedings distributed as planned.

ELECTRON BEAM IONIZATION FOR COAL FLY-ASH PRECIPITATORS

FLORIDA STATE UNIVERSITY
DOE - $163,695
7/14/78 - 7/13/80
Principal Investigator - R.H. Davis

OBJECTIVES – An initial determination is to be made of the conditions under which electrostatic precipitator performance can be improved by exploitation of the copious ionization produced by energetic electron beams ($E \approx 1$ to 2 Mev). The first phase of the program is a measurement of air ion current density saturation limits for electron beams readily available from industrial electron irradiation systems. In the second phase, a laboratory test system will be designed, constructed, and tested to optimize the conditions for electron beam utilization when the system is operating on reentrained coal fly ash of several types.

RECENT WORK AND ACCOMPLISHMENTS – In the precursor measurements,* an air ion current density was measured for a plate potential difference of 10 kv which was a factor of 50 larger than the ion current density for the space-charge-limited operation of a conventional precipitator with a potential difference of 10 kv above corona onset. The first experiments have been designed to extend the measurements up to higher voltages (~100 kv) with plate geometries comparable to those of conventional precipitators for the purpose of establishing the maximum current density for several irradiation conditions. The collector plate assembly has been modified to accommodate the higher voltages. With the recent delivery of the new power supplies, preparations for the experiments are essentially complete. Planning of the laboratory test system operating on reentrained coal fly ash is underway but requires an update review of prompt and time-integrated monitors before the system can be completely specified. Success in increasing the ion current density at a collector plate at first appears to exacerbate the high-resistivity problem met in the combustion of low-sulfur coal. While there are several alternative attacks on this problem, a novel extension of electron beam irradiation is the exposure of the deposited fly ash to energetic electrons that will modify the fly ash conductivity—an effect that has been known for decades. Preliminary measurements with solid insulating material show a reduction of resistivity of approximately a factor of 10.

PLANS FOR THE COMING YEAR – An extension of the preliminary measurements will be made to determine the air ion current density saturation limit under various electron irradiation conditions. Design of the bench-test system will make use of these results. Modular in design, the test system will be constructed incorporating a fly-ash entrainment unit, a prompt pre-treatment monitor, the test unit, and a post-treatment monitor. Measurements with this system will provide information for the design of a pilot system that more nearly replicates stack field conditions.

COMBUSTION OF COAL-METHANOL SLURRIES IN HARTMANN RESONATOR

UNIVERSITY OF SOUTH FLORIDA
DOE - $20,000; USF - $850
9/15/77 - 3/15/79
Principal Investigator - S.C. Kranc

OBJECTIVES – Methanol is an attractive alternate fuel that is clean burning and easily produced from several different feedstocks, including coal. This project is concerned with the addition of pulverized coal to methanol to form a suspension fuel similar to coal-oil mixtures. By forming a slurry, overall costs are reduced while retaining low-pollution advantages. Methanol-coal suspensions are potentially high-grade fuels with several possible applications. The Hartmann atomizer is being developed to combust the methanol-coal suspensions effectively. This device uses a supersonic gas jet and resonator to produce powerful flow oscillations. These pulsations aid in dispersing the slurry and may interact beneficially in the combustion process. It is expected that the Hartmann atomizer may be successfully applied to the combustion of other types of suspension fuels.

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*Davis, R.H. and Finney, W.C., "Ionization by Electron Beams for Use in Electrostatic Precipitators," *Energy Research,* Vol. 2, pp. 19-27 (1978).

RECENT WORK AND ACCOMPLISHMENTS – Experiments designed to evaluate methanol-coal suspensions as fuels are being conducted. The experimental facility is a stainless-steel, water-jacketed combustion tunnel fitted with observation ports. Considerable work has been devoted to the development of the Hartmann atomizer. The final configuration consists of a disk baffle incorporating the air and fuel jets with the resonator as a single unit. Stabilization of the flame front is accomplished by a secondary air flow around the baffle. The Hartmann atomizer performs well with the suspension fuel. No clogging or erosion has been observed. After mechanical grinding, coal samples are sieved to 63μ and mixed with industrial methanol. Both bituminous and lignite coals have been tested with loading that by weight ranged up to 40 percent. Continuous agitation is required to stabilize the suspension. Combustion testing is conducted at atmospheric pressure by measuring the exhaust gas temperature and the energy deposition in the cooling jacket, while other parameters are monitored. The enthalpy output is compared to the energy content of the fuel to obtain a thermal efficiency. The results of these experiments show that the combustion of methanol and coal mixtures compares well to that for methanol alone. Burning length is increased as a result of the particulate load.

PLANS FOR THE COMING YEAR – Combustion testing will continue and be further refined until the project ends. For comparison, other related suspensions will be tested also.

COAL COMBUSTION IN OPPOSED GAS-PARTICLE JET WITH REGENERATIVE PYROLYSIS

GEORGIA INSTITUTE OF TECHNOLOGY
DOE - $50,000; Georgia Tech - $4607
9/1/78 - 8/31/80
Principal Investigator - P. Durbetaki

OBJECTIVES – The burning of coal particles is the combined effect of the interlinked processes of pyrolysis, ignition, and combustion of the volatiles and char. Efficient burning of these particles requires an understanding of the various processes and their respective influence on the entire cycle. This investigation is to study the effect of regenerative pyrolysis on the combustion of coal.

RECENT WORK AND ACCOMPLISHMENTS – Equipment modification and preliminary testing were initiated with the flat-flame burner and the rapid pyrolysis apparatus during the first month of this research project.

PLANS FOR THE COMING YEAR – The regenerative pyrolysis of coal will be studied using a flat-flame burner with an opposed gas-particle jet. The work will be coupled with measurements using the lower ignition temperature and concentration apparatus. The latter will provide variable heating rates for rapid pyrolysis to generate pyrolysis gases and use these gases for characterization.

TREATMENT OF PHENOLIC WASTEWATER WITH ANAEROBIC-ACTIVATED CARBON FILTERS

GEORGIA INSTITUTE OF TECHNOLOGY
DOE - $37,800; Georgia Tech - $11,966
9/1/77 - 8/31/79
Principal Investigator - M.T. Suidan

OBJECTIVES – This research involves the development of an advanced wastewater treatment system capable of handling high-strength phenol-bearing liquid wastes. The treatment process consists of a series of anaerobic biological filters using granular-activated carbon for a contact medium. It is potentially applicable to the treatment of wastewaters produced in coal gasification processes as well as the liquid wastes generated from other coal-conversion operations. The anaerobic-activated carbon filter has the potential of providing a stable and economically attractive treatment process because of the production of a methane-rich gas.

RECENT WORK AND ACCOMPLISHMENTS — Two anaerobic-activated carbon filter systems have been constructed, tested, and in continuous operation for approximately 1 year. Initial microbial acclimation of these units were accomplished using single organic carbon sources in the respective synthetic substrates. One unit has been acclimated and operated using glucose as the only organic carbon source, while the other unit has been operated with phenol as the feed organic carbon. Extensive chemical and microbiological analyses have been performed on the systems during their startup and when steady-state operating conditions had been reached. Analysis of the data indicates complete degradation of the phenol and efficient conversion of organic carbon to carbon dioxide and methane. Comparable performance was obtained for the glucose-fed reactor. Since achieving steady-state operation of the single carbon feed source experiments, the feed substrates have been altered to examine the co-metabolism of glucose and phenol, and the degradation of higher feed concentrations of phenol.

PLANS FOR THE COMING YEAR — System operation will be continued under a varying number of loading conditions, and system performance parameters will be evaluated until the project terminates. These system performance data will be included in the final report.

SEPARATION OF PARTICLES FROM COAL-DERIVED LIQUIDS

ILLINOIS INSTITUTE OF TECHNOLOGY
DOE - $118,376
8/1/77 - 7/31/79
Principal Investigators - D.R. Wasan, D. Gidaspow

OBJECTIVES — The objective of this program is to develop improved methods of separation of coal-derived particles resulting from various liquefaction and solvent refined coal processes. The improvements will be based on inherent or modified surface-charge properties of particles. Cross-flow electrofiltration (forced-flow electrophoresis) and settling are two of the methods of separation under investigation. One of the major bottlenecks in development of coal liquefaction technology is the removal of fine solid particles after the liquefaction step. Rotary-drum pressure precoat filtration has been the most widely employed separation procedure; however, its unfavorable economics have spurred research in alternate techniques, such as settling by the addition of a precipitating liquid. The new separation method described here, together with settling (also being investigated) promises to have an impact on liquefaction technology.

RECENT WORK AND ACCOMPLISHMENTS — Based on surface-charge characteristics of coal-derived particles, a novel filtration method of removal of these particles by the application of a high-voltage (100 to 10,000 v) electric field was developed. This technique is called cross-flow electrofiltration. It is a modification of ordinary cross-flow filtration and of forced-flow electrophoresis. It is related to the common dust-removal method by electrostatic precipitation; however, it is unique in many respects and is, thus, basically a new separation method. The concept of cross-flow electrofiltration can be described as follows: A slurry enters a porous tube with a wire running through its center. The wire and the tube are connected to a source of high-voltage direct current. Suppose the particles in colloidal suspension are positively charged relative to the liquid (note that the particles plus the liquid are neutral). The central wire then is connected to the negative terminal. The positive particles will migrate toward the wire leaving a clear boundary layer near the porous tube. This clear boundary layer is now slowly withdrawn through the porous tube. There is a continuous flow of a clear liquid. After a prolonged operation, colloidal particles that stick to the central wire can be removed by gravity by reversing the polarity of the electrode. An electrofiltration system consisting of a feed pump, a high DC power supply, and a tubular electrofilter was constructed and tested using alumina particles suspended in tetralin, a proton donor solvent used in coal liquefaction processes. Clear filtrate emerged continuously from the unit in agreement with previously determined theoretical predictions. The electrofilter was tested with samples of diluted H-Coal process liquids obtained from the coal liquefaction plant in Trenton, N.J., at various electric field strengths, driving pressures, and feed rates. A surfactant, aerosol OT, was added to the slurry to increase the electrophoretic mobility of the particles. A patent application has been filed.

PLANS FOR THE COMING YEAR — The cross-flow electrofilter will be tested using liquids derived by distillation from coal slurries for dilution rather than the xylene and tetralin that have so far been used. For rational system scale-up, a mathematical model will be developed by solving the governing partial differential equations. Settling of concentrated slurries will be studied using a batch-settling column. Slurry concentrations will be determined using a gamma ray traversing analyzer. Relevant supplementary measurements, such as electrophoretic mobilities, streaming potentials, and dielectric constants, necessary to characterize particles suspended in coal-derived liquids will be made. Two-phase flow theory will be used to develop a mathematical model as an aid for data analysis.

CARBONYLATION STUDIES OF ILLINOIS COAL AND NORTH DAKOTA LIGNITE

ILLINOIS STATE UNIVERSITY
DOE - $38,000; IU - $16,506
8/1/77 - 7/30/79
Principal Investigator - R.C. Duty

OBJECTIVES — This study is to determine the solubility characteristics of Illinois bituminous No. 6 coal and North Dakota lignite after it has been finely divided (200/250 mesh and 250/325 mesh), treated with alkali metals (potassium or sodium), and pressurized with carbon dioxide for prolonged periods of time. Previous work with sodium metal at temperatures up to 150°C had produced limited solubility of 9.5 percent at 150°C. The results of this study should elucidate the feasibility of generating aromatic radical anions and phenolic anions that subsequently can be carbonylated with carbon dioxide to form aromatic carboxylic acids and *alpha*-hydroxy carboxylic acids. If highly successful, these oxygen-rich anionic sites, which are generated along the aromatic polymer chains of coal, should enhance the solubility of coal in aqueous mediums to an appreciable degree.

RECENT WORK AND ACCOMPLISHMENTS — The carbonylation studies of Illinois bituminous coal at 200°, 250°, 300°, and 350°C with sodium metal and carbon dioxide in tetrahydrofuran (THF) have been completed and illustrate a dichotomy in solubility for THF and refluxing water.

At 200° and 250°C, the coal residue gained weight, approximately 30 percent; but at 300° and 350°C, weight losses of 0.2 and 21 percent, respectively, were recorded. The carbon and sodium analyses for these residues revealed sodium-to-carbon-atom (Na-atom/1000/C-atom) ratios of 0.9, 14.0, 21.9, 21.7, 25.2, 24.6, and 22.9 for unreacted bituminous coal; and reactions at 50°, 150°, 200°, 250°, 300° and 250°C, respectively. Since the weight increased by 30 percent, and the sodium content increased by 21 percent in the insoluble residue, one concludes that the bituminous coal does have aromatic sites that react with sodium metal and carbon dioxide, but these precursor sites for carboxylic acids are not in sufficient number to render the coal soluble to an appreciable degree in refluxing water. At 350°C, a reversal in solubility from 250°C was noted—a negative 30 percent to a positive 21 percent solubility. Since the Na-atom content of the residue had decreased from 25.2 Na-atoms/1000°C atoms at 250°C to 22.9/1000 at 350°C, the solubility decrease would suggest that a greater degree of carbonylation did occur at 350°C. This carbonylation increase precipitated a solubility increase in the coal and, consequently, decreased the Na-atom content of the insoluble residue. To increase the carbonylation of bituminous coal, potassium metal was reacted with Illinois No. 6 coal at 200°C, and it caused difficulty with the safety rupture disc of the autoclave. Two reactions at 200°C were run and each blew the safety rupture disc. Unfortunately, no quantitative solubility data were obtained but the reaction products were partially recovered from the autoclave and refluxed in boiling water. The residue from the hot water was recovered and weighed 4.5 g. The water extract was extracted with benzine/ethyl ether (1:1) to remove neutral compounds and acidified with HCl to produce 1.2 g of carboxylic acids. Assuming none of the reaction mixture was lost, the 1.2 g corresponds to a 12-percent yield of organic acids. Although the entire contents of the reaction mixture had not been recovered, an acid yield of 12 percent by weight is excellent evidence that carbonylation by potassium metal is far superior for bituminous coal than sodium metal. North Dakota lignite also has been reacted with sodium metal and carbon dioxide at 150°C. The solubility of lignite at this temperature in THF and boiling water was 18.1 percent, almost twice the solubility of bituminous coal (9.5 percent). Since lignite is known to contain more oxygen sites than bituminous, this solubility increase could be the result of ether cleavages within the lignite structure that yield low-molecular-weight water-soluble species. The Na-atom/1000 C-atom ratios for unreacted lignite is 3.9 Na-atoms/1000 C-atoms while the 150°C lignite reaction of 70 Na-atoms/1000 C-atoms illustrates an eighteenfold increase. The bituminous coal experienced a fifteenfold increase.

PLANS FOR THE COMING YEAR — The insoluble residues from the sodium reactions will be analyzed for carboxylic acid content by the barium acetate technique, and total acidity by the barium hydroxide method.* Completion of the reactions with potassium metal and carbon dioxide with bituminous coal and lignite is anticipated, and subsequent total acidity and carboxylic acid determinations of their insoluble residues will be accomplished. After these results have been tabulated, a positive quantitative identification of the degree of carbonylation with potassium and sodium metal can be ascertained.

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*Schafer, *Fuel*, 49, p. 271, 1970.

COMBUSTION STUDIES OF COAL-IN-OIL DROPLETS

NORTHWESTERN UNIVERSITY
DOE - $40,000; Northwestern U - $2106
8/1/77 - 7/31/79
Principal Investigator - C.K. Law

OBJECTIVES – The burning of coal-oil mixtures (COM) in furnaces and boilers promises to be a viable short-range solution for partially alleviating the demand on petroleum oil without major combustor hardware modifications. This program aims to gain fundamental understanding of the combustion characteristics of single-COM droplets. Particular emphasis is on the characterization of the agglomeration of coal particles as the more volatile oil is vaporized off from the individual droplets. If these agglomerates are indeed formed, then they are the ones that actually undergo combustion rather than the much finer coal particles originally used, which would have important implications on coal-particle sizing, radiative transfer rate, fuel burning rate, and the size of the particulates emitted.

RECENT WORK AND ACCOMPLISHMENTS – A series of experiments has been completed on the burning of a single 800 μm COM droplet while suspended by a thin quartz fiber. The COM consists of No. 2 heating oil and various amounts of dried 200-mesh Pittsburgh seam coal powder. The droplet is ignited by spark discharge and the subsequent combustion processes observed through high-speed cine-microphotography. It is found that after ignition the droplet combustion is accompanied by intermittent ejection of small masses from the droplet, which is believed to be caused by the internal boiling of the volatile components with the coal particles serving as heterogeneous nucleation sites; however, after all the oil has been vaporized and burned, a large coal particle agglomerate is formed. The mass of this agglomerate is found to be about 80 percent of the original amount of coal addition for coal loadings of 20 percent or higher by mass. Subsequently, about 5 to 10 percent of water is added to the coal powders before they are mixed with oil. For these coal/oil/water droplets, shortly after ignition a catastrophic explosion occurs and shatters the entire droplet into much smaller pieces. This phenomenon is believed to be caused by the boiling of water, which occurs more easily than does the boiling of oil. These results suggest the following conclusions and recommendations. Initial coal powder size is probably not very critical because some degree of agglomeration will always occur even with water-induced explosion. If large agglomerates are desired for combustion from the viewpoints of enhanced radiative transfer and particulate collection efficiency, then the coal powders need to be dried before mixing. On the other hand, if small agglomerates are more desirable because of burning time considerations, then the naturally present moisture is ideally suited to induce explosion. Thus, the practice of coal drying, which requires energy, may actually be detrimental to the combustion of COM droplets.

PLANS FOR THE COMING YEAR – Completed experiments have involved droplets suspended by a fiber and burning in the cold ambiance. An apparatus has been assembled and future experiments will be conducted by spraying COM into a high-column furnace. The agglomerates formed will be collected and analyzed. The results are expected to closely resemble those obtained from actual combustor burning involving free droplets in hot environments.

RAPIDLY SOLIDIFIED NONEQUILIBRIUM ALLOYS AS CATALYSTS FOR FOSSIL-FUEL PROCESSING

SOUTHERN ILLINOIS UNIVERSITY, CARBONDALE
DOE - \$40,000
8/1/77 - 7/30/79
Principal Investigators - W. Brower, G.V. Smith

OBJECTIVES – The objective is to develop new catalytic systems for fossil-fuel conversion with emphasis on hydrogenation and desulfurization reactions. These new systems will be rapidly solidified nonequilibrium alloys made by a splat cooling technique. This technique alters the equilibrium lattice parameters and crystal structures of alloys and changes them into new catalyst systems. Nonequilibrium systems that catalyze new reactions would open new pathways for fossil-fuel conversion; on the other hand, systems that increase rates of present reactions would increase efficiencies of fossil-fuel conversion. Moreover, these catalyst systems made from low-cost raw materials would substantially lower the cost of fossil-fuel energy.

RECENT WORK AND ACCOMPLISHMENTS – Master alloys of Pd-20 a/o Si and Ni-43 a/o Au have been prepared in high-purity alumina crucibles in a newly constructed vacuum melting apparatus. Splat-cooled samples of the Pd-Si and Ni-Au alloys as well as pure Ni have been analzyed by X-ray diffraction by the Debye-Scherrer technique and by optical microscopy. Diffraction from the pure Ni splats indicates a predominantly crystalline face-centered cubic structure. A small amount of diffuse scattering could indicate a nonequilibrium glassy portion of the pure Ni splat structure; this result needs further verification. The splat-cooled Pd-Si alloy is completely glassy in X-ray diffraction, and polished cross sections of Pd-Si splat flakes refuse to etch, indicating a glassy structure. The same etch revealed the expected two-phase structure in the Pd-Si master alloy. The Ni-Au alloy exhibited a structure similar to the pure Ni, a predominantly crystalline structure, with the possibility of a small portion of glassy phase also present. The crystal structure of the Ni-Au alloy is a single face-centered cubic nonequilibrium solid solution with a lattice parameter of 3.80 Å (very close to that of rhodium, 3.75 Å, rhodium being a very active hydrogenation catalyst). The palladium-silicon glass exhibits high catalytic activity in the dissociation of hydrogen and of deuterium and in the hydrogenation and deuterium exchange of hydrocarbons. Furthermore, it produces deuterium exchange distributions similar to those produced by crystalline palladium (Engelhard 5 percent Pd/Al_2O_3). These preliminary results verify the existence of new and different catalyst systems, and also support the microcrystallite theory of short-range order in these glasses. The high catalytic activity of the palladium-silicon glass may reflect its structure; for example, if the structure is a jumble of tiny crystallites, then a large internal surface area may be available for catalysis. Similarly, small crystallites will expose a higher proportion of catalytically active edges and corners than ordinary crystalline palladium. Finally, in contrast to the few discrete interatomic distances available on crystalline palladium, the glass exhibits a wide range of interatomic distances. Some of these newly available distances may offer highly favorable geometries for the hydrogenation and deuterium exchange of hydrocarbons. The preliminary deuterium exchange results suggest the similarity of short-range order in the glassy Pd-Si splat-cooled catalyst to that of the crystalline palladium catalyst. Thus, an unexpected bonus is the potential for studying glass surface structure and possibly differentiating among the various metallic glass structural models. Regardless of which metallic glass structural model is correct, it must account for the higher catalytic activity of the glassy splat-cooled catalyst. Splats of pure Ni, the Pd-Si alloy, and the Ni-Au alloy have been vacuum aged for 24 hr at 500°C, well above the expected stability range for these nonequilibrium structures. Initial observations by optical microscopy and X-ray diffraction indicate all three splats transformed completely to the equilibrium structure. Less severe aging treatments are underway to determine the transformation kinetics of these nonequilibrium structures. Splats with the above aging treatment and resulting equilibrium structure will be compared to unaged splats in the catalytic tests.

PLANS FOR THE COMING YEAR – Based on the encouraging catalytic activity exhibited by the Pd-Si amorphous alloy, a series of nickel-based alloys will be prepared. Ni-Pd-P, Ni-Pt-P, and Ni-P all should exhibit amorphous splat-cooled structures. A comparison of catalytic results on Pd-Si, Ni-Pd-P, and Ni-P should separate the effect of the presence of Pd from the effect of the amorphous structure. Other Ni-Au alloys will be made with lattice parameters slightly less than that of rhodium to search for an optimum in hydrogenation activity similar to that observed for pure metals. A collaborative effort with Argonne National Laboratory to analyze the surface structure and composition of these splat catalysts is planned. Of special interest are possible changes in surface structures after catalytic testing and changes in surface composition after aging treatments when equilibrium surface segregation may appear.

COAL ANION STRUCTURE AND CHEMISTRY

UNIVERSITY OF CHICAGO
DOE - $183,000; Chicago U - $18,000
3/77 - 3/80
Principal Investigator - L.M. Stock

OBJECTIVES – This research involves the development of new methods for coal alkylation, the use of these methods in the preparation of isotopically labeled soluble coal compounds, the characterization of the coal compounds by nuclear magnetic resonance spectroscopy, and the development of a satisfactory theory for the coal structure that accommodates the experimental observations. The realization of this objective will provide a more secure basis for the development of reagents and catalysts for coal conversion processes.

RECENT WORK AND ACCOMPLISHMENTS – The alkylation reactions of Illinois No. 6 coal have been investigated. The Illinois No. 6 coal has been converted to a polyanion using different metal reducing agents, solvents, and electron transfer agents. The extent of electron transfer differs for these different reagents. The experimental results suggest that the less-stable more-reactive anion radicals and dianions obtained from aromatic electron transfer reagents are more effective for the depolymerization of the coal molecules. The reactions of the coal polyanion with methylation, butylation, and octylation reagents have been studied. In addition, the reactions of the coal polyanion with n-butyl chloride, bromide, iodide, p-toluenesulfonate, and trifluoromethylsulfonate have been studied. The experimental observations reveal that the sulfonate esters are too reactive for effective alkylation and that butyl iodide is the most effective reagent for the conversion of the intractable Illinois No. 6 coal to a product that is soluble in common organic solvents such as tetrahydrofuran or chloroform. Two alkylation reactions convert more than 85 percent of the carbon components of this coal sample to soluble products. The reaction of the Illinois No. 6 coal has been carried out with 90 percent carbon-13 enriched n-butyl iodide. The reaction products were separated by gel permeation chromatography. The individual product fractions were studied by proton and carbon nuclear magnetic resonance spectroscopy. The spectroscopic results for the samples enriched in carbon-13 are much more definitive than the results obtained with unlabelled reagents; for example, the carbon-13 resonances of the 0-alkylation products are clearly discernible. The 0-alkylation reaction proceeds to give aryl butyl ethers as the dominant product with some alkyl butyl ethers and alkyl esters. The analyses of these reaction products are continuing; however, initial results suggest that the extent of 0-alkylation to C-alkylation depends upon the molecular weight of the product.

PLANS FOR THE COMING YEAR — Further work on the chemistry of the alkylation reaction will be performed, with particular reference to the use of metals in liquid ammonia for the electron transfer reactions of coals having different geological origin, and the synthesis and study of other carbon and deuterium labeled reagents for the alkylation reaction to determine the character of the reactive sites in the coal molecule more definitively.

MODELING OF FLUIDIZED-BED COMBUSTOR WITH IMMERSED TUBES

UNIVERSITY OF ILLINOIS, CHICAGO CIRCLE
DOE - $89,016; Illinois U, Chicago Circle - $28,670
5/9/75 - 9/9/78
Principal Investigator - S.C. Saxena

OBJECTIVES — A mathematical model of a fluidized-bed combustor is being developed that will include coal-combustion phenomena and will incorporate basic mass transport relationships, bubble mechanics, heat transfer, and configuration effects. A cold model test bed will be designed, constructed, and operated to generate data in support of this effort. In particular, experiments will provide data concerning heat-transfer effects of tubes and tube bundles in fluidized beds, bubble formation, dispersion, and the like. The successful completion of the analytical research will provide a reliable base for the design and scale-up of fluidized-bed combustors. The experimental work will enable the calculation of heat transfer by immersed boiler tubes or their optimum design for a certain heat-removal rate from the fluidized bed.

RECENT WORK AND ACCOMPLISHMENTS — Experiments have been carried out to measure total heat-transfer coefficient for rough tubes and a smooth tube of the same outside diameter (12.7mm) immersed in a square fluidized bed (30.4 by 30.4 cm) of glass beads as a function of fluidizing velocity. In particular, tubes of four different surface roughness and glass beads of three different sizes (265, 357, and 427 μm) have been used. Comparison of results suggests that the heat-transfer coefficient strongly depends on the ratio of pitch (P) to particle diameter ($\bar{d}_p$). By the proper choice of ($P/\bar{d}_p$) ratio, the maximum total heat-transfer coefficient for V-thread tubes can be increased by as much as 40 percent over the value for a smooth tube with the same outside diameter; however, for values of ($P/\bar{d}_p$) less than 0.95, the maximum heat-transfer coefficient for V-thread rough tubes is smaller than the smooth tube for the same outside diameter. The qualitative variation of the heat-transfer coefficient for rough tubes with ($P/\bar{d}_p$) is explained on the basis of the combined effect of contact geometry between the solid particles and the heat-transfer surface, and the solids renewal rate at the surface. The total heat-transfer coefficient is measured between electrically heated horizontal tubes in a bundle arranged in staggered array and a square fluidized bed of silica sand (167 and 504 μm) and alumina (259 μm). The tubes are located at the vertices of equilateral triangles. The height of the bottom row of tubes in a bundle is kept at 132mm above the distributor plate in all experiments. The effect of particle size, mass fluidizing velocity, tube pitch, and bed height on heat-transfer rate is investigated. The maximum error in the measurement of heat transfer coefficient is estimated to be ± 6 percent; the repeatability of heat transfer measurement is ± 2 percent. The heat-transfer coefficient increases with increase in the value of fluidizing velocity. The increase is rapid in the beginning and slows down as the superficial velocity is increased. The heat-transfer coefficient attains its maximum value at some higher fluidizing velocity. The initial increase results from decrease in particle residence time at the tube surface from particle mixing caused by rising bubbles in the fluidized bed. Further, the residence time of particles decreases with increase in the value of gas velocity caused by increase in bubble-induced particle circulation; however, at larger values of gas velocity, the rate of increase of heat-transfer coefficient decreases as a result of increase in surface area of the tube, which is engulfed by rising bubbles. The effect of tube pitch between 4.5 to 9 is found to be negligibly small. The value of maximum heat-transfer coefficient, $h_{w\ max}$, for a bundle of tubes when relative pitch is 2.25 is about 5 percent smaller as compared to the value of $h_{w\ max}$ for a single tube.

PLANS FOR THE COMING YEAR – This project was completed in September 1978.

MICROSTRUCTURAL EFFECTS IN ABRASIVE WEAR

UNIVERSITY OF NOTRE DAME
DOE - $109,267; Notre Dame U - $5223
3/15/77 - 3/14/79
Principal Investigators - N.F. Fiore, T.H. Kosel

OBJECTIVES – This program is aimed at establishing quantitative relations between microstructure and gouging and low-stress abrasive wear for a number of alloys used in coal-conversion processes. The relations allow an empirical ranking of the wear resistance of the alloys, and provide the designer and materials engineer with rules, based on the principles of physical metallurgy, for the specification of materials for wear resistance. The research is being performed on cast white irons and Co-base superalloys fabricated by powder metallurgy (PM) techniques. The alloys span a range of carbide volume fractions, carbide hardnesses, and matrix properties. Both sets of materials are used for wear resistance in coal-conversion applications; moreover, they are relevant to basic studies in that their microstructures allow a systematic specification of the role of second-phase particle and matrix properties on wear. This program is based on a three-faceted experimental approach involving wear testing (low-stress and gouging), mechanical testing, and metallography (optical, quantitative, and scanning electron).

RECENT WORK AND ACCOMPLISHMENTS – Low-stress tests are performed on a rubber wheel device (RWAT) described in ASTM STP 615. Both semirounded SiO_2 sand and angular Al_2O_3 grit of average particle size (about 250 μm) are used. Gouging tests are conducted on a device (GAWT) in which a rotating bonded Al_2O_3 grinding wheel abrades samples pressed onto it by a level-arm system. The wheels are bonded from the same Al_2O_3 abrasive used in the RWAT. One result of the RWAT studies is that both the SiO_2 and Al_2O_3 abrasives break down during the course of the test, which is surprising since it was developed to simulate low-stress abrasion in which, by definition, the abrasive is unaffected by the wear process. The finding is of fundamental importance in that the theories and predictive models of low-stress abrasion are based on the assumption that the abrasive is not degraded. The observed degradation may account for shortcomings of the theories for material selection and design. The tests on the cast irons show that wear is a strong function of microstructure; for example, RWAT and GAWT tests have been conducted on Ni-Hard 4 irons of varying percentages of retained austenite (γ). In low-stress abrasion against SiO_2, wear is at a maximum at about 40 percent γ, whereas in gouging abrasion, wear is at a minimum at 40 percent γ. These findings are consistent with those obtained with other test devices at the AMAX research laboratories, and they indicate the importance of tailoring materials selection and microstructure to the specific wear application. The fact that a given microstructural feature may impart wear resistance in one application and detract from wear resistance in another is underscored by RWAT and GAWT tests on the Co-base alloys. Under gouging conditions or under low-stress conditions against SiO_2, a minimum in wear exists at intermediate carbide levels. On the other hand, low-stress wear decreases monotonically with carbide content against the hard Al_2O_3 abrasive. Scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDXS) is being used in an effort to correlate material attrition mechanisms with microstructure. Typical SEM results for a CO-base alloy, RWAT tested against SiO_2 indicate that the matrix is abraded perferentially by the SiO_2 and that the harder carbides stand out in relief. An EDXS Cr dot map clearly identifies Cr-rich carbides as the entities that resist abrasion and impact wear resistance to this alloy of rather low solid-solution strengthener content.

PLANS FOR THE COMING YEAR – The project expires in June 1979; if renewed, the overall thrust of the research will be continued with emphasis on alloy irons and PM alloys that are to be the next generation of wear-resistant materials.

CHARACTERIZING ORGANONITROGEN AND ORGANOSULFUR FUNCTIONALITIES

PURDUE UNIVERSITY
DOE - $93,800
9/78 - 8/80
Principal Investigator - R.G. Cooks

OBJECTIVES –This work seeks information on the molecular structure of coal with emphasis on the functional types in which organic oxygen, nitrogen, and sulfur occur. New methodology, which involves a mass spectrometric procedure applicable to complex mixtures, is being used. This procedure–mass-analyzed ion kinetic spectrometry (MIKES)–is based on using mass spectrometry for both separating components of mixtures and identifying individual molecular species. Pyrolysis of coal directly by MIKES should provide minimal opportunity for molecular reorganization during analysis. The chief objective of the work is to obtain access to the intrinsic molecular forms in which heteroatoms occur in coal.

RECENT WORK AND ACCOMPLISHMENTS – Preliminary studies of coal have demonstrated the feasibility of using MIKES for coal analysis. Several aromatic compounds were identified in a coal powder without sample pretreatment. Well-characterized coal samples have been obtained from the Penn State Coal Research Section to be used in all subsequent analyses. The methodology has been tested using a coal liquid sample. Fractional pyrolysis followed by chemical ionization (proton attachment) has yielded MIKE spectra identical to those of azaphenanthrene and other known constituents of the sample. The high sensitivity and compound specificity of MIKES plus the ability to analyze small quantities of complex mixtures without chromatographic separation or chemical pretreatment is thus seen to be uniquely promising. The detection specificity for organonitrogen compounds in a complex coal liquid test mixture has been enhanced by development of a special scanning technique. In this technique, molecules that readily lose an electron are preferentially sampled. An analogous detection specificity enhancement is also expected for organosulfur compounds. These scanning techniques can be directly applied to the analysis of organonitrogen and organosulfur compounds in coal. Computer equipment to facilitate coal data acquisition and storage has been specified and is in the process of being procured. The feasibility of computer control of the MIKES analyzing magnet has been demonstrated, and a circuit module allowing routine computer control is under construction.

PLANS FOR THE COMING YEAR – With the use of well-characterized coal samples of varying rank and organosulfur contents, a systematic study of chemical ionization mass spectra will be undertaken. These spectra will be obtained under varying pyrolysis conditions, and ions that differ greatly in the spectra of low- and high-sulfur samples will be the focus of MIKES studies. Identification of the constituents responsible for these ions will be attempted, using the MIKE spectra of authentic materials for comparison and structural elucidation. A parallel set of experiments will use varying ionization methodologies, including negative chemical ionization, to pinpoint compounds of potential interest for MIKES studies. Again, the identification of individual heteroatom-containing molecules will be the prime objective. The instrument itself will be developed further to facilitate the acquisition and reduction of an increasing volume of MIKES data, which involves computer control of the mass and energy analyzers.

GASIFICATION IN PULVERIZED COAL FLAMES

PURDUE UNIVERSITY
DOE - $208,491; Purdue U - $6254
9/75 - 1/78
Principal Investigator - N.M. Laurendeau

OBJECTIVES – The feasibility of using available pulverized coal burners to produce power (or synthesis) gas from coal is being investigated. The configurations to be considered are the annular confined jet with secondary swirl and the slagging vortex tube with tangential entry. Both reactors are designed to achieve efficient gasification via fuel-rich combustion or axial injection of preheated steam. Gasification of coal to synthesis and power gases is an economically and environmentally attractive means of expanding coal usage. This investigation is primarily concerned with the formation of a clean low-BTU gas from coal. Entrained flow methods are emphasized owing to their high volumetric reaction rates, low tar formation, and acceptability of caking coals and slurries.

RECENT WORK AND ACCOMPLISHMENTS – The gasification facility flow, heating, control, and temperature monitoring systems are installed and in working order. The reactant gas flow meters, coal feeder, and product gas analysis system, which consists of a water cooled probe and a mass spectrometer, have been tested and calibrated. Typical coal flow rates are 7 to 28 lb/hr with O_2/coal ≅ 0.7 to 1.4 and H_2O/coal ≅ 0.0 to 0.6. Design and construction of both the cyclone and confined jet gasifiers are complete. Methane combustion experiments have been carried out in both reactors to confirm the reliability of the torch ignitors and the product gas analysis system. A computer program that calculates the important independent and dependent performance parameters from the raw exhaust data has been written for both coal combustion and gasification. Of particular importance are the carbon cold gas, and hot gas efficiencies. In a series of coal combustion tests and a fuel-rich gasification test without steam addition carried out in the cyclone reactor, reactor stability was excellent over a range of equivalence ratios from 0.67 to 2.4 and air flow rates from 70 to 210 lb/hr. Typical carbon efficiencies were 92 percent for air-rich and stoichiometric tests and 80 percent for gasification tests. At 50 percent stoichiometric air, the cold and hot gas efficiencies peaked at 50 and 75 percent, respectively. The product gas heating value was 75 btu/scf and the carbon efficiency was 85 percent. A macroscopic model for coal combustion and fuel-rich gasification in the cyclone has been developed. The fluid mechanics are modeled by a particle force balance and a series combination of a perfectly stirred reactor and a plug flow reactor. Kinetic treatments of coal pyrolysis, char oxidation, and carbon monoxide oxidation are included. A gas-phase equilibrium treatment is used for the gasification case; gas composition and temperature are also checked against equilibrium values. The model predicts exhaust gas composition, carbon efficiency, cold gas efficiency, and hot gas efficiency. Comparison between theory and experiment is quite good.

PLANS FOR THE COMING YEAR – The cyclone model will be used to predict the optimum design characteristics for gasification with and without steam addition. Experiments will then be conducted for various reactor designs to confirm these predictions while maintaining slagging operation. Any inconsistencies are expected to foster improvements in both the model and the cyclone. Coal-combustion and fuel-rich gasification tests will be conducted in a manner similar to the cyclone gasifier using the macroscopic model. Internal probing will be initiated in both reactors to optimize chamber design and further model development. These models can then be used for gasifier scale-up.

INVESTIGATION OF CROSSLINKED POLYMERIC NATURE OF BITUMINOUS COALS

PURDUE UNIVERSITY
DOE - $99,998
9/1/78 - 8/31/80
Principal Investigator - N.A. Peppas

OBJECTIVES – The program reexamines the physical behavior of entanglements and crosslinks in bituminous coals to explain technical problems faced in coal extraction. The main objectives are to develop a theory for a modified Gaussian model of rubber elasticity, which could be applicable to highly entangled and structurally complex macromolecules such as those observed in coal structures; to modify statistical thermodynamic theories and obtain an accurate method of prediction of the degree of crosslinking in coal; establish experimentally the swelling behavior of coal in solvents and/or swelling agents of varying thermodynamic interaction parameter χ, and to measure the latter one; to use these data to calculate the crosslinking density of various coal samples and compare these findings to the predictions of the theoretical models; and to explain the effect of various coal structure parameters on the physical behavior of coal. It is anticipated that this novel theoretical and experimental analysis will elucidate phenomena and physical behavior observed during solvent coal extraction and will explain the varying extractability of coal samples of the same chemical but different physical structure.

RECENT WORK AND ACCOMPLISHMENTS – Laboratory equipment is being procured or adapted for setup at Purdue's Macromolecular Chemistry and Engineering Laboratories. Various types of bituminous coals are also being procured from the Coal Research Laboratories of Pennsylvania State University. Finally, theoretical work was started on the development of a statistical mechanical model for the behavior of highly crosslinked macromolecules, not usually described by the Flory theories.

PLANS FOR THE COMING YEAR – Thorough analysis of the crosslinking structure and its effect on the physical behavior of coal will be done using a range of experimental variables including four coal particle sizes and various size distributions, C and H percent composition of coal, type and purity of the solvent and/or swelling agent, temperature of swelling, and chemical structure of the coal samples. At least 15 coal samples of varying C and H content will be investigated using four solvents. The coal samples will be extracted in modified extraction columns to remove the extractable solvent-soluble coal portions, which will be analyzed for molecular weight distribution using gel permeation chromatography. The nonextractable coal matrices will be dried *in vacuo* and used for swelling and sorption studies in a novel electromicrobalance setup. The swelling data cannot be used for quantitative analysis of the crosslinking density before the determination of the χ thermodynamic interaction parameter; therefore, membrane osmometry studies will be initiated to determine the Flory χ-factor for coal-solvent pairs at various temperatures. Preliminary analysis of the experimental data will be carried out in preparation for the final modeling and additional experimental analysis.

CREEP BEHAVIOR OF MONOLITHIC REFRACTORIES

IOWA STATE UNIVERSITY
DOE - \$119,450
3/1/78 - 2/28/80
Principal Investigators - T.D. McGee, J.R. Smyth

OBJECTIVES – Practical utilization of coal gasification hinges on the availability of adequate refractory linings for process vessels. Refractory concretes based upon aluminum oxide and alumino-silicate aggregates and calcium-aluminate cements will assume a major role in meeting these refractory needs. Possibly the most important single factor affecting the use of these concretes is creep behavior over extended periods of time. The purpose of this project is to evaluate the short- and long-term creep behavior of monolithic refractory concretes as related to composition and microstructure, and more specifically to determine the creep mechanism(s) in these materials. Also the data obtained during this project will be used in the stress-strain mathematical model DOE has developed for its program on refractories for coal conversion.

RECENT WORK AND ACCOMPLISHMENTS – Modifications of the two existing creep-testing instruments for loads up to 3000 lb have been completed. Twelve composite creep experiments were performed on materials from Babcock and Wilcox (B&W). A composite creep experiment (which takes 6 to 10 days, and in some cases 30 days) consists of loading a specimen at several temperatures between 1000° and 2200°F while using the same level of stress throughout the experiment. Typical stresses are between 1000 and 2500 psi. The materials consisted of a 90+ percent Al_2O_3 dense castable, a 50+ percent Al_2O_3 dense castable, and an insulating castable. Results were compatible with other B&W experiments. A 90+ percent Al_2O_3 and a 50+ percent Al_2O_3 dense generic refractory concrete is being prepared in house. Creep experiments have been performed on these generic castables and on neat cement specimens of CA-25C, Secar 71, and Refcon calcium-aluminate cements. Porosity and density data were obtained before and after creep to determine what effect the stress and temperature conditions have on the specimens. Creep experiments on the concretes have shown that strain rate is negligible for low temperatures and stresses, but relatively rapid strain rates are exhibited as the combination of temperature and stress is increased. Extreme conditions cause the specimen to exhibit tertiary creep, which ultimately leads to catastrophic failure. Creep experiments on the pure cements indicate that the cements creep substantially more than the concretes at the same conditions. It is believed that the cements control the creep behavior of these refractory concretes.

PLANS FOR THE COMING YEAR – More creep experiments are needed to characterize these refractories. The creep data will be analyzed to determine stress exponent (n) and activation energy (ΔH_c) parameters for these castable refractories. Further analysis will be required to determine what creep mechanisms are present. Modulus of rupture (MOR) tests will be performed on the castables at varying water and cement contents to determine optimum compositions. Creep tests will then be done to correlate MOR results with results from the creep experiments. DTA and X-ray tests will be used to gain a better understanding of the hydration process. Microstructural analysis will be done on specimens before and after creep, using light microscopy and SEM to determine structural changes that result from temperature alone and from combinations of temperature and stress.

SEMIFLUIDIZED-BED FILTERS FOR COAL PROCESSING

KANSAS STATE UNIVERSITY
DOE - $45,091; KSU - $15,213
9/1/78 - 8/31/80
Principal Investigator - L.T. Fan

OBJECTIVE – The physical nature of the semifluidized-bed filter is such that the control of "cake thickness" is accomplished without the use of complicated mechanical devices such as cutting blades. This program evaluates the applicability of semifluidized-bed filters to the filtration of coal wash water and liquefied coal. The dependence of throughput capacity, specific resistance of the filter, total pressure drop, and effluent clarity on different modes of operation will be determined. Theoretical and statistical analyses of the experimental data will eventually lead to the identification of optimal design and operating parameters.

RECENT WORK AND ACCOMPLISHMENTS – Two semifluidized-bed filters are being assembled. The particle-size distributions of coal dust and other particulate systems to be used in this study are being measured. Bed packings of various sizes are being procured. Other preliminary work involves the preparation of a state-of-the-art review on semifluidization.

PLANS FOR THE COMING YEAR – The state-of-the-art review will be completed. Filtration of coal/water slurry under ambient temperature and low-pressure conditions will be performed with the semifluidized-bed filters. Measurement of filter capacity, filter resistance, overall pressure drop, and effluent clarity and their temporal variation under a restricted model of operation will be undertaken. The results of the experiment will then be compared to the performance of conventional filters.

CATALYTIC ACTIVITY OF COAL MINERAL MATTER

UNIVERSITY OF KENTUCKY RESEARCH FOUNDATION
DOE - $107,510; Kentucky U - $22,098
1/1/76 - 7/31/79
Principal Investigator - C. Hamrin

OBJECTIVES – The objective is to determine the ability of naturally occurring mineral matter found in coal to desulfurize and denitrogenate catalytically model sulfur- and nitrogen-coal compounds. A pulse microreactor connected to a gas chromatograph is the reaction system to be used. Mineral matter is to be obtained by low-temperature ashing of coal in an oxygen plasma. All liquefaction processes under development, catalytic or noncatalytic, add hydrogen to coal containing mineral matter. Depending on the process, hydrogen is added to increase the H/C ratio of the product and/or to remove heteroatoms such as S, N, and 0. Successful completion of this study will rank the mineral matter of eight to ten U.S. coals in ability to desulfurize and denitrogenate model S and N compounds. In addition, the importance of the individual components and synergistic interaction among them will be determined. Modification of activity by mild chemical treatment and during either the SRC or SRL process will also be measured. The importance of mineral matter catalytic activity will have process implications in determining catalyst quantity and desirability of recycling mineral matter as in the SRC-II Process.

RECENT WORK AND ACCOMPLISHMENTS – Nine coals were selected and low-temperature ash samples were prepared. Characterization of the LTAs by X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis, BET surface area, and pore volume was completed. X-ray diffraction of raw coal samples was also carried out to show that little if any change occurred during low-temperature ashing. The catalytic activity for thiophene HDS at equal final catalyst weights and for n-butyl amine HCS is as follows (at 400°C and 1 atm):

HDN	
LTA	Percent Conversion
Kentucky No. 11	54.9
Kentucky Homestead	48.3
Illinois No. 6	42.2
Elkhorn No. 1	36.0
Bruceton	33.3
Pitts. Seam (Ireland)	33.3
Kentucky No. 9	17.1
Clearfield	14.6
Lignite	1.4

Surface area for HDN also gave the highest correlation followed by the Si and K concentrations. To eliminate the effect of surface area, the HDN results were put on an equal area basis. Correlations were obtained slightly below the 95 percent confidence level for A1, Si, and Ti. The effect of chemical treatment with HCl, H_2O, KCl, and other solutions on the activity was determined. No significant improvement was found for the former three, but a patent application has been filed for a treatment that increased HDS activity 45 times but left HDN virtually unchanged. SRC processing appears to have a detrimental effect on mineral matter activity. Mineral matter in Kentucky Nos. 9—14 feed coal to the Fort Lewis pilot plant was more active than that in the mineral residue. Iron sulfide catalysts of high surface area (41 m^2/g) and varying S/Fe were prepared by sulfiding hematite under different time, temperature, and gas compositions. The highest conversion of thiophene was found at an atomic ratio of S/Fe = 0.78. LTA pyrite was also found to have significant HDS activity although its surface area was only 2.4 m^2/g.

PLANS FOR THE COMING YEAR — Final work on this contract will be completed by the end of July 1979.

ANALYSIS OF DESIGNS FOR COAL-CONVERSION PRESSURE VESSELS

UNIVERSITY OF KENTUCKY
DOE - $246,699; Kentucky U - $17,302
3/1/77 - 2/28/80
Principal Investigators - D.C. Leigh, T.R. Tauchert

OBJECTIVES — A comprehensive study of alternative structural designs for large-diameter pressure vessels for various coal gasification and liquefaction processes is being conducted. Alternate designs are being analyzed and evaluated critically on the basis of structural integrity, reliability, safety, manufacturing parameters and constraints, and optimized and compared on the basis of minimum overall cost. The work consists of the following tasks: Task I—Definition of Pressure-Vessel Needs; Task II—Preliminary Design and Analysis (an evaluation and comparison of many types of structural-materials designs and a selection of a few of the most feasible); Task III—Advanced Design and Analysis (detailed designs will be done for selected combinations of structural designs and processes); Task IV—Evaluation of Limiting Constraints; Task V—Determination of Manufacturing and Other Costs; Task VI—Design Optimization (on the basis of total minimum cost, subject to constraints, and shall consist of two facets: the selection of optimum structural-material combinations corresponding to the given sets of pressure vessel needs, and the optimization of the selected structural-material combinations); and Task VII—Recommendations.

RECENT WORK AND ACCOMPLISHMENTS — The basic information in Task I has been obtained from the literature. A structural classification of pressure vessels has been defined and briefly described. Visits to fabricators, organizations, and technical society meetings concerning various kinds of structural designs for pressure vessels has been largely accomplished and documented. Information on the following pressure vessel structures was obtained: single-wall, shrunk fit, concentric layered arcs, spiral layered arcs, prestressed concrete, prestressed cast iron, spiral sheet, helically wound interlocking strips, filament wound, fluid layered, and girth ringed. A design for a prestressed cast-iron pressure vessel (PCIV) for coal gasification was prepared by the Siempelkamp Company of Krefeld, West Germany, for use in this project. Much of Task II, Preliminary Design and Analysis, is complete except for the detailed comparison of the various types of pressure-vessel construction followed by the selection of the most feasible designs for each combination of process and diameter. Certain tentative general selections have been made. For large-diameter and pipeline gas pressure, a construction other than single-wall steel will have to be used; for example, concentric or spiral-layered arcs, prestressed concrete, or prestressed cast iron. For diameters of about 10 ft and liquefaction pressures, the layered constructions including shrunk fit and spiral sheet also appear feasible. Computer programs for the determination of stresses caused by elastic and thermal effects in cylindrical layered walls have been adopted and some sample calculations done. The formulation of exact and approximate methods of stress analysis for cylindrical vessels under stationary, nonaxisymmetric temperature distributions is underway. Consideration is being given in this study to temperature-dependent behavior, anisotropy, and the effects of creep. The results of the investigation are being used in Task III, Advanced Analysis and Design.

PLANS FOR THE COMING YEAR – Detailed designs will be done for selected combinations of structure and process. The optimization of structural designs for Task VI, Design Optimization, will be done for those cases in which significant optimization can be achieved. The remaining tasks, including Task VII, Recommendations, will be completed.

SURFACE STRUCTURE AND MECHANISMS OF GASIFICATION CATALYST DEACTIVATION

UNIVERSITY OF KENTUCKY
DOE - \$394,286; Kentucky U - \$175,286; United Catalysts, Inc. - \$77,131
2/1/76 - 12/31/79
Principal Investigators - P.J. Reucroft, E.B. Bradley, R.J. DeAngelis, G.A. Sargent

OBJECTIVES – This research program seeks to obtain a detailed understanding of the factors governing the high specificity of nickel-based catalysts in methanation reactions; characterize and obtain a better understanding of the microscopic phenomena that lead to deterioration of catalyst performance through chemical poisoning; evaluate the validity of accepted models of catalyst thermal deactivation; and use the information obtained from the basic research program to design new catalyst systems with improved activity, selectivity, resistance to poisons, and thermal stability compared to available commercial catalysts.

RECENT WORK AND ACCOMPLISHMENTS – Significant conclusions from the project can be summarized as follows: In coprecipitated alumina- and silica-supported nickel catalysts, a high fraction, ranging from 20 to 70 percent depending on the catalyst, of the active metal (nickel) is complexed with the support material in a difficult-to-reduce spinellike form. In the case of magnesium-silicate-supported nickel catalysts, the support interactions appear to be much less. The higher methanation activity observed in heavily sulfide magnesium-silicate- and magnesium-aluminate-supported nickel-chromium catalysts may be associated with the formation of sulfate in competition with sulfide in these systems. $CO + H_2$ adsorption on Ni(III) at 300°C creates an intense Raman band at 80 cm^{-1} when observed using 4880 Å exciting radiation. The surface species that is adsorbed appears to be similar to a cyclic hydrocarbon and is very stable with respect to thermal decomposition (150° to 400°C). Auger studies showed that the adsorption of CO on a sulfur-contaminated catalyst sample surface was slow. The sticking coefficient was $<3 \times 10^{-3}$, the adsorption of CO probably proceeding through the substitution of S and O on the active site of nickel. Studies of the temperature and pressure dependence of the interaction of CO with a sulfur poisoned Ni(111) surface have indicated the presence of two CO adsorption states; dissociated and nondissociated. At high temperatures (100°C), pyrolysis of CO takes place resulting in the formation of a carbidelike species on the surface. The thermal-sintering behavior of supported nickel catalysts can be followed by determination of the changes that occur in the particle-size distribution function from X-ray diffraction data. Particles of NiO and nickel in coprecipitated catalysts have been found to contain appreciable microstrains. In coprecipitated $NiO\text{-}Al_2O_3$ and $NiO\text{-}SiO_2$ it is necessary to use hydrogen chemisorption data combined with TGA data to determine the average metallic particle size. Excellent agreement with X-ray measured particle sizes is then obtained.

PLANS FOR THE COMING YEAR – ESCA studies, useful in determining average catalyst particle size and in studying sintering effects, will continue on magnesium-silicate- and magnesium-aluminate-supported nickel and nickel-chromium catalysts. These studies will also be extended to include nickel-rare earth catalysts prepared by impregnation on the same supports. Further studies on the relationship between ESCA signal intensities and metal particle size will be initiated. The sintering studies will be extended into longer time regimes. The laser Raman studies and the LEED/Auger studies on the interaction of carbon monoxide at nickel single-crystal surfaces will be closely coordinated to gain more information on the nature of the carbon complex that forms on the metal surface. It is anticipated that the surface characterization studies will be coordinated with the catalyst preparation and testing activities that are in the planning stage at the Kentucky Center for Energy Research Laboratory.

HOT GAS DESULFURIZATION

UNIVERSITY OF KENTUCKY
DOE - $155,158; Kentucky U - $40,926
4/1/76 - 3/31/79
Principal Investigator - J.T. Schrodt

OBJECTIVES – This project seeks to develop and critically evaluate a high-temperature, coal-derived fuel gas desulfurization process that uses gasifier coal ashes as sulfur sorbents. Efforts are focused on gathering bench-scale sorption data and formulating models suitable for the preliminary design and analysis of both fixed- and fluid-bed systems. A comparison of high- and low-temperature fuel gas usage in combined-cycle gas turbine and steam-boiler power plants indicates higher efficiencies can be achieved using hot fuels. Gasifier technology has progressed to the stage of full development and demonstration; however, further R&D on high-temperature fuel gas desulfurization is required.

RECENT WORK AND ACCOMPLISHMENTS – Fifty-eight desulfurization-regeneration fluidized-bed bench-scale tests were completed using Western Kentucky No. 9 gasifier ash. These tests were conducted on 151- and 194-μ-mean diameter particles at 900° to 1400°F and at atmospheric pressure. They demonstrated the feasibility of the fluid-bed mode for desulfurization of fuel gases. Most of the tests were carried out at twice the minimum fluidization velocity, and with 1 percent H_2S in the influent stream. Many of the findings from the fixed-bed studies were confirmed by the fluid-bed tests. Sulfur capacity of fresh ash increased and stabilized after 10 to 12 cycles. A maximum capacity of 315 grains of H_2S/lb of ash at 1200°F was determined. Gas bubbles in the bed were very small, thereby validating the assumption of plug-flow of gas. Critical evaluation of the data is incomplete. A computer program was written and tested for simulating a steady-state combined desulfurization-regeneration fluid-bed process, but full implementation of the program awaits reduction of the test data.

PLANS FOR THE COMING YEAR – Work will focus on completing all experiments and evaluating the fluid-bed data. The project will conclude with a simulation study of a steady-state process.

INVESTIGATIONS OF ENHANCED OIL RECOVERY USING CARBON DIOXIDE

LOUISIANA STATE UNIVERSITY
DOE - $161,120
7/7/78 - 7/6/80
Principal Investigator - W.R. Whitehead

OBJECTIVES — The efficacy of carbon-dioxide flooding and modified carbon-dioxide flooding as enhanced oil recovery techniques will be studied in the laboratory. The experimental work will be carried out in slim-tube sand packs and 2-in.-diameter consolidated sandstone cones. The results of this investigation should lead to new or improved carbon-dioxide flooding techniques that will increase oil recovery in reservoirs that are amenable to carbon-dioxide flooding.

RECENT WORK AND ACCOMPLISHMENTS — Laboratory equipment for conducting the carbon-dioxide flooding is being constructed. A gas chromatograph has been procured to facilitate these analyses. Column designs and analysis techniques are being perfected. Also being procured are representative Gulf Coast and Permian Basin Crude Oils for study.

PLANS FOR THE COMING YEAR — The construction of the carbon-dioxide flooding facilities will be completed. Displacement experiments in the slim-tube sand packs will begin in the near future. The first displacements will use a synthetic oil in order that the experimental procedures and sampling techniques can be perfected. Subsequent displacements will use actual crude oils. When the consolidated-core flooding equipment is completed, some of the displacements studied in the slim-tube sand packs will also be studied in the consolidated cores allowing the determination of the effect of water saturation on recovery mechanisms. There will also be some PVT work performed to support the displacement experiments.

BOUNDARY-LAYER PROFILES IN MHD GENERATORS

BOSTON UNIVERSITY
DOE - $50,000
9/1/78 - 8/31/80
Principal Investigator - T.M. Fang

OBJECTIVES — The boundary-layer effects in the channel of an MHD generator are being studied, with emphasis on the thermal instability phenomenon. By performing perturbation to heat-balance equations, the construction phenomenon in the boundary can be understood. Also, by taking electron-impact ionization and recombination processes into account, the fluid equations will be modified. More correct boundary-layer profiles in MHD channel can then be found.

RECENT WORK AND ACCOMPLISHMENTS — By collecting and analyzing MHD channel performance data, serious boundary-layer thermal effect—mainly in the form of arcing instability—has been noticed. Basically, the heating process is naturally caused by the Joule heat, and cooling is done by forced connection and probably radiation in the channel. Heat conduction becomes important only at the wall of the channel. By rewriting the heat balance equation and assuming the constricting processes will form current-carrying columns in cylindrical shapes, the thermal instability phenomenon in the MHD boundary layers has been studied in detail. The current-carrying column problem is being analyzed in one dimensional radial coordinate. Only the transversal component is studied and the column is assumed symmetric in all directions on the cross-sectional plane. Radiation and conduction are neglected. This analysis turns out to be so powerful that many arcing parameters including the arcing temperature can be predicted, and a general instability criterion has been established that allows not only the electrical conductivity dependence, but also the variation of many other heat-transfer parameters (such as the connective coefficient and the radius of the constricting column). Naturally, the previous arcing criterion becomes just one special case of the general model.

PLANS FOR THE COMING YEAR — Work on the thermal effect study will be continued. More heat transfer mechanisms will be included, and the analysis may be expanded to two or even a complete three-dimensional geometry. Also, the current fluid equations used in MHD channel work will be investigated and modified so that the electron-impact reaction can be taken into consideration properly.

MODELING OF FLUIDIZED-BED COMBUSTION OF COAL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $1,250,511
2/1/78 - 1/31/80
Principal Investigator - J.F. Louis

OBJECTIVES — This project has two main objectives: first, to establish a comprehensive system model sufficiently precise for use in process and engineering design optimization; secondly, to establish a data base management system (DBMS) for repositing all relevant data on coal-based fluidized-bed combustors (FBC) in a single site that can be used to answer various queries from remote sites. The system model could also be used as a system assessment tool and, hence, a useful adjunct in the planning of experimental programs. As a result of recent developments in this project, it now appears that the DBMS can independently (i.e., without help from models) furnish designers with a set of powerful design tools.

RECENT WORK AND ACCOMPLISHMENTS — The initial system model consisted of four state-of-the-art component models selected for initial application: fluid dynamics – fast bubble model, combustion – modified Davidson model, heat transfer – modified Vreedenberg model, and desulfurization – Borgwardt model. Each component model was critically examined and modified, and replacement of the entire component by a new model was found to be necessary. The interim model now consists of: fluid dynamics – two-region model, combustion – substantially modified Davidson model, heat transfer – new model, and desulfurization – new model. Design curves derived from this interim model with respect to combustion efficiency and sulfur capture have been found to yield reasonable and useful results. The FBC-DBMS consists of four major elements: a parent DBMS with 1200 variables, a much smaller DBMS with 75 variables, a set of empirical equations, and a set of transparent application programs. A "scatter plot methodology" is being developed that could provide FBC designers with a means for determining the numerical magnitude of design parameters based solely on stored data.

PLANS FOR THE COMING YEAR — Although the computed parameters from the interim model appear reasonable, its simplistic nature must be fully recognized. In addition, a number of model assumptions are not verified; thus, a second-pass improvement should lead to a more complete and comprehensive system model. The immediate goal is to develop a system model that can predict the following parameters: minimum fluidizing velocity, expanded bed height, exchange coefficients, carbon loading, combustion efficiency, SO_2 emissions, stone utilization, CO emission, NO_x emission, heat-transfer coefficients, and bed temperature. Development of data base file structure, input program, and application programs will continue. The "scatter plot methodology" will be fully developed and implemented. Attempts will be made to input the plant data when they become available to the DBMS on a semiautomatic basis.

COMPUTER-AIDED INDUSTRIAL PROCESS DESIGN

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $3,285,000
6/1/76 - 5/31/79
Principal Investigator - L.B. Evans

OBJECTIVES — The goal of the project is to develop a computer-based process simulator and economic evaluation system for use in the engineering of fossil energy conversion processes. The system, Advanced System for Process Engineering (ASPEN), will be used by DOE to provide a rapid, efficient, and consistent means of performing its process evaluation functions. Because of the large expenditures for fossil energy process development, it is important to identify problems early, before beginning costly construction of pilot and demonstration plants. ASPEN will contain data bases for the physical properties of coal and routines for modeling solids-handling operations and waste-product recovery systems. It will also be compatible with chemical reactor models currently available or being developed. The system will provide both detailed heat and material balances and detailed economic projections for process plant construction and operation over its entire economic life. The results computed will include cost of products, capital and operating cost, and return on investment. ASPEN's 150,000-line program will be entirely in FORTRAN for easy transportability to different computers. Strict standards of program design and documentation are used for ease of updating and maintainability. Industry representatives from 50 leading chemical, fossil energy, and construction companies serve on an advisory committee along with experts from Government and universities. Senior staff members have been recruited from industry to work directly on the project.

RECENT WORK AND ACCOMPLISHMENTS — Major progress has been made toward system implementation. Functional specifications, describing in detail what ASPEN would do, were reviewed by the advisory committee and used to develop design specifications specifying in detail how the functions would be implemented. By the end of September 1978, system coding was approximately 75 percent complete. A major industrial simulator system, FLOWTRAN, was purchased and installed for project use. FLOWTRAN, developed by Monsanto, is one of the leading industrial process simulators for conventional vapor-liquid systems. The calculation programs of FLOWTRAN will be modified and incorporated into ASPEN. Numerous nonproprietary programs have been acquired and other proprietary programs are being negotiated for acquisition.

PLANS FOR THE COMING YEAR — ASPEN is scheduled for completion in October 1979. Coding of all subsystems, as well as integration and testing with the full ASPEN system, and user and system documentation will be completed. To demonstrate how ASPEN would be used by a fossil energy development team, three benchmark simulations will be performed on a Lurgi gasification process, a donor solvent liquefaction process, and a fluid-bed combustion process. Plans are being formulated for a second phase of the project involving use and testing of the system by Government and industry users.

COMBINED-CYCLE RESEARCH

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $733,461
7/1/76 - 7/1/79
Principal Investigators - J.F. Louis, J.F. Elliott

OBJECTIVES — Analytical and experimental research is being conducted to support the development of gas turbine-steam combined-cycle power plants with overall efficiency and operation cost advantages over contemporary power plants. This basic research program addresses three critical and highly coupled problems affecting the allowable inlet gas temperature to the turbine stages of the gas turbine engine, using combustion products of coal-derived fuel as the working fluid: turbine cooling, materials corrosion, and fuel gas desulfurization. This work will provide essential data for gas turbine component design and will therefore serve as a vital complement to the DOE High-Temperature Turbine Technology Program. This effort will also supply corrosion data for other metal and ceramic components and necessary data on the optimal characteristics of dolomite for desulfurization at high temperature.

RECENT WORK AND ACCOMPLISHMENTS — A cascade test section using a representative airfoil operating at combined-cycle conditions was built, and data were obtained for determining heat transfer and pressure distribution around an uncooled blade. A new high-temperature section has now been added to the blowdown facility and a test section was designed for conducting film cooling experiments in adverse pressure gradients such as those occurring in advanced industrial gas turbines. Results of analytical studies on the heat transfer and fluid dynamics in partially filled water coolant channels for high-temperature turbine blades have provided design criteria for nucleation and burnout in high-speed liquid films and the stability of thin films. Flow visualization experiments on such water films in a recently constructed rotating channel facility revealed a fairly regular wavy structure of the thin film, whose surface became irregular as the Reynolds number and rotational speed were increased. Another test facility, for conducting closed-loop water cooling investigations in a rotating simulated coolant channel, has yielded sufficient data for a proposed correlation for the critical heat flux. Factors that affect the solubility and rate of dissolution of alumina in molten sodium sulfate are being studied. Kinetics of dissolution have been measured at 927°C and show the process to be first order. The effects of small additions of tungsten oxide in molten sodium sulfate on the rate of corrosion of alumina were measured. Electrochemical measurements using small additions of molybdenum oxide or of vanadium oxide indicate that V_2O_5 is even more acidic than either MoO_3 or WO_3 at the same concentrations in their respective solutions with Na_2O. A recently built thermogravimetric apparatus is being used to study the reaction of SO_3 in the gas phase with liquid sodium sulfate and liquid sodium sulfate-tungsten oxide solutions. The surface tensions of molten sodium sulfate and potassium sulfate were measured. Studies have been made of sulfidation and regeneration of calcined limestones and dolomites (natural and synthetic) that are well characterized in terms of calcite, dolomite, and magnesite contents, and morphology (crystallite sizes, surface areas, and pore size distribution). A procedure for producing synthetic dolomites of a range of Ca/Mg ratios was developed. The experimental data on the desulfurization rates of synthetic dolomites has been compared with different theoretical models.

PLANS FOR THE COMING YEAR — Experimental work in the high-temperature blowdown facility concerning turbine cooling with an air film will be completed. Analytical studies and experimental work in the liquid cooling facilities will continue, with the rotating full-channel closed-loop tests focusing on the effect of simulated coolant tube diameter on the proposed critical heat flux correlation. The rotating open-channel liquid-film-cooling test rig will continue with flow visualization, augmented by actual measurements of film thickness. Additional data will be obtained on the solubility and the rates of dissolution of alumina in molten sodium sulfate to determine the mechanism of attack of alumina by pure sodium sulfate and the effect of small amounts of tungsten oxide or molybdenum oxide, including the effect of temperature. The solubility and rate of dissolution of chromia in molten sodium sulfate will be studied. Measurements of the activity of Na_2O in Na_2-MoO_3 melts will continue. Thermodynamic measurements will be extended to include the WO_3-SO_3-Na_2O system. Experimental studies using synthetic dolomites for high-temperature desulfurization will center on the change in performance of the stones as a function of cycling between sulfidation and regeneration.

BASIC STUDIES OF COAL PYROLYSIS AND HYDROGASIFICATION

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE $292,191
1/1/77- 1/31/79
Principal Investigator - J.B. Howard

OBJECTIVES – The objective of this research is to obtain improved fundamental understanding of the conversion of coal to clean fuels by processes based on rapid pyrolysis and hydropyrolysis. Specific tasks are to measure compositions and rates of formation of products from the pyrolysis and hydropyrolysis of a partially dried Montana lignite and a Pittsburgh Seam bituminous coal under systematically varied conditions including heating rates (270° to 10,000°C/s), pressures (0 to 100 atm of hydrogen, helium, and mixtures thereof), final temperatures (400° to 1100°C), and particle sizes (5 to 1000 μm), using small-scale batch and entrained-flow reactors. Other objectives are to develop correlations and predictive models from the experimental data and to determine the distributions of original sulfur and nitrogen in product chars. This research is important to fossil energy technology since pyrolysis in inherently a very high thermal efficiency method of coal conversion while hydropyrolysis at short-residence times holds great potential for production from coal of large yields of high-quality liquid and gaseous fuels.

RECENT WORK AND ACCOMPLISHMENTS – A comprehensive experimental study of product compositions from the pyrolysis and hydropyrolysis of both coals was completed using the batch reactor. Extensive work was devoted to interpreting these findings including development and refinement of kinetic models of pyrolysis and documentation of the resultss. Specific findings include marked differences in the pyrolysis behavior of these two coals with the dominant volatile products from the bituminous coal being tar and light hydrocarbon liquids, while carbon oxides and pyrolytic water are most prominent for lignite. Pressure and particle size exert little effect on product yields from lignite, but for bituminous coal under rapid heating conditions and above 800°C, increases in either parameter decrease the yields of tar and hydrocarbon liquids and increase the yields of methane, hydrocarbon gases, and char. Heating rate had negligible effect on total yields or product distributions. The pyrolysis data are consistent with a correlation between CO_2 evolution and the estimated carboxylic oxygen content of the raw coal and between pyrolytic water evolution and estimated hydroxyl oxygen content. Kinetic analyses show that the evolution of different products from lignite is successfully modeled by one, two, or three first-order decomposition reactions. For bituminous coal, a similar model modified to include pyrolytic evolution of tar followed by competition between its transport by evaporation and diffusion and its destruction by secondary cracking is found to be broadly consistent with observed effects of pressure and particle size. Use of these data and models to calculate the heating value and surface flux of volatiles under conditions pertinent to pulverized coal combustion indicates, in agreement with previous work, that combustion on the particle surface may in some cases precede the occurrence of volatiles flame away from the surface. Experiments on the rapid pyrolysis and hydropyrolysis behavior of bituminous coal under entrained flow conditions were completed using the laminar flow reactor. For an estimated heating rate of 10^4°C/sec and solids and volatiles residence times of 0.5 sec, total volatiles and gas yields for pyrolysis at 1 atm of helium increase with temperature from 600° to ~800°C, but tar yields decrease steadily above 600°C. Secondary cracking reactions of volatiles are believed to exert a significant influence on final product composition above 900° to 1000°C. Preliminary studies of sulfur and nitrogen evolution under helium and hydrogen at pressures from 1 to 4 atm (abs.) were also completed with the flow reactor. Broad trends include a reduced retention of sulfur and nitrogen in product chars as temperature increases, with this effect being modestly enhanced in hydrogen at temperatures above 700° to 800°C. Exploratory studies on the effect of particle diameter in the range 15 to 33 μm were also completed for these conditions.

PLANS FOR THE COMING YEAR — Work will continue on analysis of rapid hydropyrolysis data including development of improved kinetic models. Further studies of particle diameter effects on the disposition of sulfur and nitrogen will also be performed.

COAL PYROLYSIS BY HOT SOLIDS FROM FLUIDIZED-BED COMBUSTOR

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $119,995; MIT - $10,000
6/1/77 - 5/31/79
Principal Investigator - J. Longwell

OBJECTIVES — The objective of this research is to determine the technical feasibility of generating relatively clean, economically storable gaseous and liquid fuels by the fluidized-bed pyrolysis of coal in the presence of dolomitic solids capable of in situ H_2S and CO_2 removal. Specific tasks are to measure yields of gaseous, liquid, and solid products; gas compositions; and sulfur and nitrogen contents of chars and liquids from at least two coals of commercial importance. Pyrolysis is carried out in a fluidized bed (2-in.- I.D.) in the presence and absence of three dolomitic stones under conditions of practical interest including bed temperature (800° to 1600°F), total pressure (1 atm), coal feed rate (0.3 to 5 lb/hr), dolomite-to-coal weight ratio (0 to 50), coal and dolomite particle-size distributions (250 to 500 μm), and fluidizing velocity (0.6 to 1 ft/sec). Related objectives are to develop global correlations and predictive models using these data.

RECENT WORK AND ACCOMPLISHMENTS — Systematic studies of the pyrolysis behavior of Illinois No. 6 bituminous coal and Texas lignite in the presence of sand and three dolomitic stones have been completed. Preliminary analysis of the lignite results support the approach:

	800°F		1400°F	
	Sand	Dolomite	Sand	Dolomite
Percent of coal heating value in:				
Gas	6.6	8.8	12.8	16.2
Tar	14.2	12.4	12.9	8.6
Char	59.4	53.6	59.1	55.3
Vol percent of H_2S in gas	4.6	<(1 ppm)	3.5	<(1 ppm)
Vol percent of CO_2 in gas	26.0	0.8	17.7	11.9
Gas HHV (Btu/ft^3)	698.7	935.0	507.8	591.6

At temperatures from 800° to 1400°F, elimination of H_2S and other vapor phase sulfur compounds occurs when the lignite is pyrolyzed with dolomitic stones. Further, at the lower temperature, the volume percentage of CO_2 in the product gas is reduced from 26.0 in the sand case to 0.8 when pyrolysis is performed in the presence of dolomite. One of the most striking results is that, over the stated temperature range, the use of dolomitic stones in pyrolysis results in increases of 25 to 35 percent in the fraction of the coal heating value in the gas and of 15 to 35 percent in the gas volumetric heating value. These effects reflect CO_2 removal and an augmented make of hydrocarbons, the latter apparently resulting in part from increased post-pyrolysis cracking of tar by the dolomitic stones. Despite a reduction in absolute yield, the tar appears to be of a higher quality with a lightly elevated H/C ratio than that from the sand case; however, there was very little effect of dolomite on the tar sulfur and nitrogen content.

PLANS FOR THE COMING YEAR – Work is continuing on the analysis and interpretation of the product yield and composition data for both coals. Thermodynamic calculations will be performed to assess the approach of the gas compositions to equilibrium at various temperatures, and a model based on the two phase theory of fluidization will be used to predict product gas compositions at the exit of the 2-in.-I.D. reactor. Some preliminary estimates of the economics of process gas production by this process will be made.

FUNDAMENTAL STUDIES OF PHYSICO-CHEMICAL PROPERTIES OF COAL SLAGS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $183,889
9/28/77 - 9/27/80
Principal Investigator - J.F. Elliott

OBJECTIVES – This program is developing from sources in the literature information on the physico-chemical properties of constituents to be found in various types of coal slags. The data being extracted are important for determining the nature of corrosion of ceramic and metallic materials that may be exposed to the combustion gases and slags in coal-fired systems, and the amounts and types of very fine inorganic particulate matter that may be carried in the off-gases from these systems. Principal attention is being directed to the oxides of minor constituents that are found in coal slags and to silica.

RECENT WORK AND ACCOMPLISHMENTS – Attempts are being made to use current theories of the structure of liquid silicates in predicting the thermodynamic properties of minor constituents in acidic liquid oxides (slags). Very limited information is available on the properties of alkali oxides in glasses, phase diagrams of silicate systems containing these alkali oxides, and the structural theories. Predictions cannot be made from structural considerations alone for liquid oxides that are typical of acidic coal slags, because the structural elements of these slags are not known; therefore, parameters are being sought relating to the polymerization of the silicate tetrahedra in these slags that can be evaluated from known thermodynamic properties. A capability is being developed for an interactive assessment using computer facilities to assist in analyzing, interpreting, and producing thermodynamic data. The aim is to produce tables of data and correlation equations of those data for use in large computers for combustion calculations; programs based on data used in preparing the JANAF Tables are being used, and the JANAF form of tables will be one of the results of the analyses of data. Programs to produce correlations in the form needed for the various combustion calculation packages are also in use.

PLANS FOR THE COMING YEAR – Available data on oxide compounds and various structural models will be used to find some empirical means of estimating such properties as the oxygen ion concentrations in acidic slags. This step is important to the possibility of estimating the physicochemical properties of many of the constituents in these slags. Work will continue on developing an interactive computer system to analyze and collate thermodynamic properties of chemical species to be found in coal slags.

MEDIUM- AND HIGH-TEMPERATURE GAS CLEANUP OF PARTICULATES

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $279,932
9/77 - 9/79
Principal Investigators - J.Louis, J. Melcher

OBJECTIVES – This research program is an experimental investigation of the applicability of the electrofluidized bed (EFB) and other related devices to the collection of particulate products of coal combustion at elevated temperatures. Bench-scale experiments will span the range of 400° to 1800°F covering conventional utility, fluidized-bed combustion, gasifier, and combined-cycle system operating regimes. Major goals include the investigation of novel techniques of charging fine particles, experimentation with various electrode geometries, quantification of energy usage trends with increasing temperature, and identification of appropriate EFB "sticking agents" to prevent elutriation of collected particulate matter.

RECENT WORK AND ACCOMPLISHMENTS – The test rig has been constructed and interfaced to monitoring instrumentation. Shakedown tests have been completed, and initial experimentation has begun. The test rig is capable of producing 120 acfm at 1800°F. Natural gas burners supply the hot gases that pass through the EFB. Particulate matter is redispersed into the hot air stream at the bottom of the experiment by an auger feeder-venturi injector combination. The dust-laden gas stream proceeds upward where it can be diluted to the desired temperature. This gas is isokinetically sampled using Andersen impactors or absolute filters to determine the particulate loading and characteristics of this simulated effect. After sampling, the particulate matter is charged, either by being passed through a corona flux or by a novel technique. The corona flux is created by a point to plant geometry by a stainless-steel mesh with points at high voltage. The charged particulate matter is passed to the EFB or an electropacked bed. Essentially, these devices are beds of semiconducting granules such as sand or dolomite that are either in a fluidized or packed condition. An electric field is applied across these beds, polarizing the bed material. The charged particulate is attracted to the appropriate side of the polarized bed particles and collected. After passing through the bed, the gas stream is sampled again to determine outlet loadings and size distributions. This experiment has been instrumented and interfaced to the MIT Energy Laboratory computer, which prints a status report of temperatures at the combustor, charger, bed wall, and in the freeboard region. Pressure drop across the bed and relevant voltages, currents, and volume flow rates are also reported. A window in the bed section permits visual examination of the fluidized or packed bed.

PLANS FOR THE COMING YEAR – The high-temperature limits to corona charging will be explored. Methods of charging by using a flame as an ion source will be investigated. Voltage-current curves will be taken for electrofluidized and electropacked beds to predict their energy usage characteristics at high temperatures and to study mechanisms of charge transfer in these devices. Research toward finding an appropriate sticking agent for EFBs will be continued.

FACTORS AFFECTING FATIGUE CRACK GROWTH IN LOW-ALLOY PRESSURE-VESSEL STEELS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DOE - $373,418
7/27/78 - 7/26/81
Principal Investigator - R.O. Ritchie

OBJECTIVES – The object of this investigation is to examine subcritical propagation by fatigue of small cracks subject to steady and cyclic loads in thick-section pressure-vessel steel plate, involving mechanical, metallurgical, and environmental factors pertinent to high- and low-BTU coal gasification plants. The materials selected for study are candidate steels for the coal gasifier pressure vessel, namely thick section plate of SA387-2-22 (normalized 2 1/4 Cr-1Mo), SA542-2 and -3 (quenched and tempered 2 1/4 Cr-1Mo), SA516-70 (normalized C-Si), and A543-1-B (quenched and tempered NiCr-Mo), in both base metal and weld areas. The experimental research will concentrate on characterizing fatigue crack propagation behavior from pre-existing flaws at ultra-low (near-threshold) growth rates below 10^{-8}m/cycle in inert, air, hydrogen gas, and simulated coal gasifier environments. In service, such growth may arise from high-cycle, low-amplitude stresses generated from small pressure and temperature fluctuations (termed "operational transients") that are expected to occur during "steady-state" operation as a result of real variations in coal feed rate, "clusters" of pulverized coal, combustion instabilities, and pressure fluctuations in feed and discharge gas lines.

RECENT WORK AND ACCOMPLISHMENTS – Preliminary work to develop a mechanical test system for fatigue testing that permits reproducible measurement of crack growth rates down to 10^{-11} m/cycle has been completed. The system uses a high-frequency electro-servo-hydraulic testing machine with crack monitoring achieved by a highly sensitive electrical potential technique. Thick section plates of SA387, SA542, and SA543 have been procured, and are being characterized with respect to microstructure and mechanical properties as a function of plate position. Initial near-threshold fatigue crack propagation testing in SA387 (base metal) in ambient temperature air has shown that whereas yield strength is very sensitive to plate position, near-threshold growth rates are largely unaffected. Crack propagation behavior in this steel is being investigated as a function of mean stress in both air and hydrogen gas environments.

PLANS FOR COMING YEAR – In association with the Lockheed Palo Alto Research Laboratories, experimental characterization of near-threshold fatigue behavior in SA387 and SA542 will continue in atmospheres of vacuum, air, and hydrogen to define the environmental contribution to cracking. Experiments are planned to examine the influence of prior temperature embrittlement on cyclic growth rates in SA387, and the effect of differing microstructures induced by variations in cooling rates on growth rates in SA542. Tests systems will be developed for near-threshold crack growth rate testing at temperatures between ambient and 350°C in hydrogen gas, hydrogen plus hydrogen sulfide, and simulated coal gasifier environments.

MODEL FOR REFRACTORY CONCRETE LINER–ANCHOR INTERACTIONS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
6/8/77 - 5/31/79
DOE - $122,893
Principal Investigator - O. Buyukozturk, J.J. Connor

OBJECTIVES – The objectives of this work are to develop an understanding of the effect of stainless steel anchors on single- and dual-refractory liners of cylindrical coal gasification vessels during heatup and cooldown; predict the resulting stress and strain distributions, which may lead to degradation processes such as cracking and creep; and to recommend optimum heating schedules, material properties combinations, and anchor spacings to avoid local degradation caused by anchor-refractory-liner interaction. To achieve these objectives, several tasks are planned: develop a three-dimensional nonlinear analysis capability for the thermomechanical analysis of anchor refractory-liner interaction in the cylindrical coal gasification vessels (the analysis capability will be developed on the basis that the mechanical and the heat transfer effects are uncoupled; perform a parametric study of the effects of heating rates, geometrical parameters, anchor spacings, and material properties; predict the likelihood of cracking or crushing and likely cracking patterns for various anchor configurations; and make recommendations on optimum heating schedule, materials properties combinations, and anchor spacings to avoid local degradation of the refractory liners in the vicinity of the anchors; obtain the necessary material properties for developing the model from Babcock and Wilcox (B&W) personnel involved in other DOE work; and using this model, aid Babcock and Wilcox personnel with interpreting experimental data.

RECENT WORK AND ACCOMPLISHMENTS – The computer program, ARC (A Computer Program for the Three-Dimensional Finite Element Analysis of Reinforced, Prestressed, and Refractory Concrete Structures), developed for the analysis uses a time- and temperature-dependent material, nonlinear, three-dimensional finite element procedure. The refractory concrete material data obtained from B&W personnel is combined, formulated, and incorporated into the program. The analysis procedure adopted in the program accounts for the interaction between anchors and the refractory linings, progressive cracking of the refractory concrete, and for other nonlinearities caused by compression behavior, creep, and shrinkage. Three sets of mechanical analyses were performed with the model; three test runs for the verification of the computer program, with the results from these runs being compared with those from exact solutions; preliminary analyses of a representative segment of the dual-component circular coal gasification vessel including the effects of an idealized anchor in the analysis model; and simulation of two experiments performed on Lining No. 3 by B&W. Exploratory studies were conducted for heat-transfer capability. Two available heat-transfer computer programs were examined and their results compared with experimental data to determine the applicability of these programs as complementary to the mechanical analysis program, ARC. For heat transfer in the vessel model, 13 test runs were performed. Various combinations of cracks and anchors were tested using two different geometries.

PLANS FOR THE COMING YEAR – Work is in progress for both the mechanical and the heat transfer analyses of the vessel model. Further parametric studies are planned on improved computer models with anchor shapes spacings and various heating schedules. Continued efforts are being made to improve the modeling of the refractory material behavior. In this respect, an experimental program is being planned jointly with B&W for testing selected refractory concrete specimens in biaxial compression.

STUDIES FOR STABILIZING COAL-OIL MIXTURES

TUFTS UNIVERSITY
DOE - $205,669
8/78 - 7/80
Principal Investigators - G. Botsaris, Y. Glazman

OBJECTIVES – The objective of this program is to determine a rational basis for the selection of additives to impart stability and desirable rheological properties to coal-oil mixtures (COM). A method to evaluate the mean polarity (hydrophilicity/hydrophobicity) of the surfaces of different coals is being developed. Based on these and other data, a correlation is to be developed to relate the surface characteristics of different coals to their stability and rheological behavior in slurries of No. 6 oil. This investigation will lead to an understanding of the mechanism(s) of COM stabilization. Moreover, a method for characterization of the mean polarity of coals would also be useful in other coal preparation and utilization operations where surface phenomena are prevalent.

RECENT WORK AND ACCOMPLISHMENTS – The bound-rubber test, used to characterize the mean surface polarity of different types of carbon blacks, is being investigated to characterize the mean polarity of different coals. Results from preliminary tests using lignite and bituminous coal appear promising, but additional data are required to completely evaluate the application of this test for coal. Methods to characterize both the sedimentative and aggregative stability and also rheological properties of COM are being developed and are being tested on COM prepared from different coals with and without chemical additives. Results suggest that COM may be characterized as one of three types: sedimentatively unstable but aggregatively stable, and intermediate between the first two types.

PLANS FOR THE COMING YEAR – Development of the bound-rubber test is to be completed, with results used to select chemical additives—either surface-active agents and/or polymeric materials for a specific type of coal or lignite to produce a slurry of the desired stability (sedimentative or aggregative) and rheological behavior. The stability and rheological character of these COM will be specified by a two-parameter system consisting of a Gelation Number and an

Aggregation Number, which will then be correlated to the mean surface polarity of the coal. The intent is that if the mean polarity of a coal is known, the proposed correlation could then be used as a basis of selecting a suitable additive for an oil slurry without performing extensive empirical testing.

KINETICS/MECHANISMS OF CATALYTIC HYDROLIQUEFACTION AND HYDROGASIFICATION OF LIGNITE

WORCESTER POLYTECHNIC INSTITUTE
DOE $142,500
9/77 - 9/80
Principal Investigators - A.H. Weiss, W.L. Kranich

OBJECTIVES — Basic chemical kinetics and mechanisms in catalytic hydrogenation of lignite suspended in a carrier oil in a continuous reactor operating at steady state are being investigated. Specifically, the research is designed to study the overall conversion rate and the elemental transformations from the raw materials into products under surface reaction controlling conditions, and to postulate the reaction paths of hydroliquefaction and hydrogasification of lignite based upon the results obtained. From the results, a better understanding of continuous processes for lignite and coal conversion may be obtained that may lead to an improved ability to predict the behavior of pilot or demonstration plants under altered operating conditions and possible directions for process improvements.

RECENT WORK AND ACCOMPLISHMENTS — Equipment design has been completed and construction virtually finished. In the process under study, ground lignite, powdered catalyst and carrier oil are mixed in a slurry preparation tank. The slurry is transferred continuously by means of a high-pressure pump through a heated tube and thence to the reactor. Hydrogen and water (steam) are separately preheated and fed to the reactor, a 1-liter, magnetically stirred cylindrical vessel provided with electric heaters capable of maintaining reactor temperature under continuous-feed conditions. Mixed product is cooled, then flows to a high-pressure receiver where gas is separated from liquid-solid slurry and passed through a reducing valve. The slurry flows through a reducing valve into a flash pot from which additional gas is removed. After further cooling, the slurry is collected as a product. The two gas streams are mixed and passed through continuous CO_2 and CO analyzers and a gas chromatograph. After flow measurement in a wet test meter, the gas product is vented. The slurry product will be partially separated and characterized by filtration, several extractions, and gas and liquid chromatography. Analytical procedures are under development. Sufficient lignite has been ground in a jet mill in a steam atmosphere to provide uniform raw material for all of the projected runs.

PLANS FOR THE COMING YEAR — The effect of several process variables on the overall rate of conversion and on the yield of gas and liquid products will be studied. Preliminary investigation will lead to selection of a preferred oil medium, hydrogen donor solvent, and catalyst. A systematic study will then be undertaken on the effect of: temperature over the range 350° to $450^{\circ}C$, pressure over the range 500 to 1500 $lb/in.^2$, and feed rates over the range 0.5 to 4 liquid hourly space velocity. Products will be partially characterized by a combination of selective solvent extraction and both gas and liquid chromatography. Qualitative results will lead to an improved understanding of the conversion process. Quantitative results will be interpreted in terms of kinetic constants for a reaction model.

IN SITU SHALE OIL REFINING

UNIVERSITY OF MASSACHUSETTS
DOE - \$49,680; Massachusetts U - \$57,812
9/1/78 - 8/31/80
Principal Investigator - J.R. Kittrell

OBJECTIVES – This program is designed to examine the potential for in situ oxidation and the applicability of hydrogenfree ex situ refining of shale oil for removing sulfur and nitrogen heteroatoms from shale oil. The study involves oxidizing shale oil produced from a simulated in situ retorting process by contacting it with a model oxidizing agent—nitrogen dioxide—at low temperatures and atmospheric pressures; extracting the oxidized sulfur and nitrogen compounds with several polar solvents to effect a reduction of the heteroatom content in the shale oil; and characterizing the shale oil at each step of the process to determine extents of reactions and byproduct formation relevant to process commercialization. Examinations will be made of operating conditions that are relevant to: promotion of oxidation simultaneously with the in situ retorting process and ex situ refining, which gives more flexibility to select conditions most favorable to oxidation of the heteroatoms. Although catalytic hydroprocessing of shale liquids is well known, little research has been directed at hydrogenfree refining techniques for shale oil at moderate temperatures and pressures, which could improve economic, environmental, and water-use costs of shale oil refining. To use an in situ refining step simultaneously with the retorting operation could further contribute to savings in energy utilization, capital investment, and operating costs associated with hydrogen consumption and hydroprocessing catalyst.

RECENT WORK AND ACCOMPLISHMENTS – Preliminary work performed includes receipt of a sample of simulated in situ shale oil (from the DOE Laramie Energy Technology Center) that is being characterized; specifically, "fingerprinting" is underway with both low- and high-resolution gas chromatograph. Evaluations of gross compound classes are being initiated, including determinations of alkane/alkene ratios, shale acid content, basic and neutral nitrogen compounds, and sulfur compound classes. Reactor and extraction equipment is being assembled. A Dohrmann total nitrogen and total sulfur analyzer has been purchased and a gas chromatograph-mass spectrometer with a sulfur-specific detector is on order.

PLANS FOR THE COMING YEAR – An evaluation will be made of the oxidative capabilities of nitrogen dioxide at in situ (e.g., 300° to 500°C) and ex situ (e.g., 30° to 200°C) conditions. Initial screening experiments will be conducted using 0.1 to 10 percent nitrogen dioxide and 1 to 10 percent oxygen in a batch reactor with offgas chromatographic capabilities. Gross oxidation rates will be monitored with a nitrogen oxide chemiluminescence analyzer. Extraction of the oil, before and after oxidation, will be conducted with excess methanol to measure sulfur and nitrogen reduction in the raffinate. Sulfur and nitrogen material balances around the reactor will be performed to confirm analytical methods and to define offgas decomposition products containing sulfur and nitrogen. Additional solvents will be examined to define those showing promise for extraction of oxidized sulfur and nitrogen compounds in shale oil. After these screening experiments, data on rates of oxidation of shale oil heteroatoms will be taken and correlated as a function of relevant experimental variables. These data will provide information relative to the structure of the reaction and the functionality of the solvent for use in assessing the applicability of in situ and ex situ oxidation and the commercial potential of the process concept.

SLURRY COAL ASH ANALYZER FOR CONTROL OF COAL CLEANING PROCESSES

MICHIGAN TECHNOLOGICAL UNIVERSITY
DOE - $50,000; Michigan TU - $7775
9/78 - 8/80
Principal Investigator - S.K. Kawatra

OBJECTIVES — A system for on-line analysis of ash in coal slurries is being developed incorporating sensors, using low-energy gamma ray sources that will excite the coal slurry. A suitable mathematical model will then be built to correlate the ash content of the coal slurries and signals from the sensors. Coal samples will be obtained from an operating coal processing plant. They will be collected over time to assure adequate variation of particle size, chemical composition, and the like. A slurry test rig will be designed, fabricated, and tested. This rig will have the ability to be directly installed in a coal preparation plant.

RECENT WORK AND ACCOMPLISHMENTS — All work has been of a preliminary nature. The theory involved has been examined and proven practical. Laboratory equipment is being procured and/or adapted.

PLANS FOR THE COMING YEAR — The test rig will be designed using available facilities and fabricated in the Department of Metallurgical engineering, where it will be extensively tested to assure reliability and durability for industrial use. Mathematical models will be built for correlating signals from the radiometric sensors and ash content. To stimulate the whole system, computer programs will be written and an optimum design for sensors will be developed. A coal processing plant will be visited to study the particle-size variations and chemical compositions of different streams. After studying these variables, suitable slurry samples for the experimental work will be collected. Plans for future installation can be examined with personnel of the plants.

PHYSICAL AND CHEMICAL BEHAVIOR OF COAL-DERIVED LIQUIDS

UNIVERSITY OF MICHIGAN
DOE - $378,768; Michigan U - $13,982
9/30/76 - 7/31/79
Principal Investigator - D. Briggs

OBJECTIVES — The objective is to study the physical and chemical behavior of coal-derived liquids. The interactions between various fractions of coal-derived liquids, solvents, mineral matter, and catalysts will be experimentally measured to provide solubility, colloid behavior, adsorption, viscosity, and surface tension data for the design and operation of coal liquefaction processes. Model compounds will be synthesized and examined in combinations to simulate properties of coal liquids. These research results will provide a greater understanding of the physical and chemical behavior of coal as it is liquefied and of the products of coal liquefaction. The anticipated data should contribute to the design and operation of future coal liquefaction pilot and demonstration plants, especially in setting the process conditions in the preheater-reactor and solids separation.

RECENT WORK AND ACCOMPLISHMENTS — A number of alkanebisphenols and alkanebispyridines were synthesized and the compounds used in a study of their solution viscosity and hydrogen bonding tendencies. Asphaltenes were subjected to several methods of acid-base fractionation, the most successful involving formation of perchloric salts of the basic components and aryloxyacetic acid derivatives of the acid components. Equivalent weight titrations of the derivatives were effected to determine the number of reactive functionalities per molecule. Filter cake compressibility and the effect of asphaltene concentration were determined for model coal liquefaction slurries at 232°C. A liquefaction product slurry from the H-Coal process was characterized as to chemical nature and filtration behavior. The material was used in several filtration improvement studies. Precipitating solvents (toluene, tetralin, n-decane and Soltrol 130) were added to yield 0 to 20 weight percent concentrations at 121°, 167° and 232°C. Substantial specific cake resistance reductions were observed in all cases. These reductions corresponded to an increase in size of the particles making up the filter cake. The filtrate viscosity was also reduced at all additive concentrations. Four hydrogen-bonding solvents—ethanolamine, λ-picoline, 2 ethoxyethanol, and m-cresol—were found to reduce the H-Coal product filtrate at viscosity at 60°C. Filtrate viscosity and specific cake resistances of the H-Coal product slurry were measured at 121°, 167° and 232°C with the additives at 1 to 5 percent concentrations. Each additive decreased the filtrate viscosity but also increased the specific cake resistance. Melting point measurements were made on oil and resin, asphaltene, preasphaltene, and THF insoluble residue fractions from the liquefaction of an Illinois No. 6 coal in the H-Coal process. Melting point measurements were also made on combinations of the four fractions to determine relative effects. Viscosity measurements were made on the oil and resin, asphaltene, and preasphaltene fractions over a range of temperatures and shear rates.

PLANS FOR THE COMING YEAR — The colloid micelle size of asphaltenes and preasphaltenes over a concentration range in various solvents will be measured by small angle X-ray experiments. Some preliminary work will be conducted with a laser system. Filtration experiments will be conducted to determine the effect of holding time and mixing conditions on the viscosity and specific cake resistance when precipitating solvents and/or filter aids were added to liquefied coal slurries. Work will continue on developing procedures for separating asphaltenes and preasphaltenes into acidic and basic fractions and for determining the phenolic oxygen and basic nitrogen content of the fractions. The viscosity of a number of characterized asphaltene and preasphaltene samples will be measured over a range of temperatures and shear rates. The data will be analyzed to determine the principal variables for the prediction of the viscosity of liquefied coal with and without mineral solids.

GASEOUS DETONATIVE FRACTURE OF POROUS MATERIALS

UNIVERSITY OF MICHIGAN
DOE - $50,000; Michigan U - $2803
9/78 - 8/80
Principal Investigator -C.W. Kauffman

OBJECTIVES — During winter months in the northern geographical regions, coal freezes into a rigid mass while being transported in open railroad hopper cars. Considerable energy may be expended in attempting to thaw these cars or imported liquid fuels may be substituted until the arrival of warmer weather. In situ coal gasification and shale oil retorting and enhanced oil and gas recovery require an increased permeability of normally occurring strata. The use of solid high explosives leads to intense local shattering that may even decrease porosity, while liquid high explosives present substantial safety hazards. Combustible gaseous mixtures mixed in situ are inexpensive, capable of producing a constant controlled-strength impulse throughout an arbitrary volume, and present few handling difficulties. Controlled fracturing of the bed may be achieved to enhance its flow characteristic—either as the flowing material itself or the matrix through which a fluid passes. In addition, the locally developed high temperatures within the detonation may provide a thermal treatment of the matrix enhancing the release of the fossil fuel component. It is the purpose of this research program to determine the degree of fracturing that may be achieved by gaseous detonations in these porous beds.

RECENT WORK AND ACCOMPLISHMENTS — All material necessary for the construction of the experimental apparatus has been ordered and is in the process of assembly including the 1.83 m by 0.15 m double extra-heavy-steel pressure vessel. The porous packing material in the form of steel grinding balls, ball bearings, and glass marbles has been obtained. Equilibrium calculations have been carried out to determine Chapman-Jouguet conditions for hydrogen, methane, actylene/oxygen, and air mixtures. A literature survey has uncovered work pertaining to the attenuation of a shock wave in a porous bed.

PLANS FOR THE COMING YEAR — The pressure vessel will be packed with various materials and detonation parameters will be measured for different gases. Analytical efforts will be initiated to calculate the effect of energy losses on wave properties and the stresses exerted on the bed resulting from wave propagation. The impulsive mechanical loads placed on the pressure vessel will be measured, and if time allows, the effectiveness of the bed in quenching fully developed detonations will be examined.

RHEOLOGY STUDIES OF COAL OIL SLURRIES

WAYNE STATE UNIVERSITY
DOE - $40,000; Wayne SU - $23,301
9/1/77 - 8/31/79
Principal Investigators - S. Carmi, K.A. Kline

OBJECTIVES — The main objectives of this investigation are to: develop a practical method for determining the rheological properties of coal-oil mixtures under various concentration and temperature ranges and determine precombustion atomization characteristics of the mixtures for different pressures and nozzle configurations. Addressing these objectives will help characterize the slurry to enhance early detection of instability followed by corrective action for improved atomization and combustion efficiency. These objectives are aimed at developing a novel and direct coal utilization process in which a suspension of pulverized coal in oil is burned in packaged oil-fired boilers.

RECENT WORK AND ACCOMPLISHMENTS — An integral part of the fundamental rheological study is the development of a non-Newtonian fluid model with an appropriate constitutive equation. Samples of stable coal-oil slurries have been prepared in the laboratory, with coal concentrations ranging from 30 to 50 percent by weight. Extensive rheological data were obtained using capillary and cone and plate viscometers for all five samples of coal-oil slurry and No. 6 fuel oil, which served as a reference fluid. The temperature range was 130° to 180°F covering a wide range of shear rates (2 to 2500 $\sec^{-1}$). Viscosity measurements show coal-oil slurries to be shear thinning suspensions; that is, the viscosity decreases moderately with increasing shear rates. At the concentration range of 30 to 40 percent coal, the slurry shows a predominantly Newtonian behavior. For slurries with concentrations higher than 40 percent coal, a yield point ranging from 5 to 20 dyne/cm^2, depending upon the sample and test conditions, is observed. Shear thinning effects also start to be evident. In addition, rheological properties are being studied using a rotating rod viscometer constructed for this project. The study of these samples of coal-slurries with the rotating rod viscometer indicates migration of coal particles away from the rotating rod with no noticeable rod climbing, and thus, no evidence of normal stress effects.

PLANS FOR THE COMING YEAR — A laboratory test bench will be designed and built for the investigation of spray formation and precombustion atomization. A flow control unit equipped with various nozzles will be followed by a glass chamber through which the slurry jet spray will be discharged into a storage tank. The chamber will be photographed during the spray discharge for characterization at various pressures and flow rates, and the storage tank will be equipped with an exhaust system. Rheological findings will be related to the characteristics of slurry atomization and spray formation in various nozzles and for different parameters (e.g., pressure) values.

FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

WESTERN MICHIGAN UNIVERSITY
DOE - $178,724; Western Michigan U - $28,302
6/11/75 - 9/29/80
Principal Investigator - T. Houser

OBJECTIVES — The objectives of this research program are to obtain rate and product distribution data from which a mechanism may be proposed for the formation of nitric oxide from fuel-nitrogen during the combustion of coal and heavy oils. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) are being studied. In addition, similar oxidative studies are being made on representative condensed-ring heterocycles to determine the extrapolatability of the results obtained for pyridine to more coal-like structures. The oxidation of volatile nitrogen-containing pyridine pyrolysis products is being carried out to help elucidate the mechanism of nitric oxide formation. Study results will be useful in models of nitric oxide formation during combustion.

RECENT WORK AND ACCOMPLISHMENTS — Experiments using the stirred-flow reactor to obtain differential rate data were continued. The results have been divided into two categories: those dealing with inert pyrolysis and those involved with oxidation. The rate of pyrolysis of pyridine was found to be described by first-order and autocatalytic terms in the rate equation. A chain mechanism was developed for the pyrolysis that was consistent with the first-order term and with the primarily nonvolatile product formed. The rate of evolution of HCN, the major nitrogen-containing pyrolysis product, indicated that the formation was subsequent to the decomposition of the pyridine, presumably caused by further degradation of intermediate species. Thus, the rate of disappearance of the reactant is not an adequate measure of the rate of formation product. The catalizing agent in the pyrolysis has not been identified and work is continuing on this mechanism. Oxidation experiments have been performed with pyridine, acetonitrile, and vinyl cyanide as the fuel with the following results: If the reaction mixture is fuel rich, no NO is formed (mass pysectrometer monitoring, observing the 30 m/e ion) for all three fuels; when the reaction mixture is oxidizer rich, the size of the 30 ion is much larger for pyridine than for the other two fuels — acetonitrile appears to yield the least; the yield of NO appears independent of temperature for all three fuels. A chemiluminescent NO-NO_x analyzer has been ordered with a special adaptation that will allow determination of NH_3 also.

PLANS FOR THE COMING YEAR – Pyrolysis work will concentrate on identifying the catalytic agent in the decomposition of pyridine and on observing what influence it may have on the rate of formation of HCN. The oxidation work will focus on determining under what condition NO/NO_x is formed from pyridine, H_2 - $(CN)_2$ mixtures, and vinyl cyanide and the rate of their formation. The reaction variables of interest are concentration (oxydizer/fuel), reaction times, and temperature. It is believed that H_2 - $(CN)_2$ mixtures will simulate HCN chemically and be safer to handle in the laboratory than HCN. From these results, it will be possible to predict how the pyrolysis of fuel will influence the evolution of NO during combustion.

LOW-BTU COAL GASIFICATION TECHNOLOGY IN OPERATIONAL ENVIRONMENTS

UNIVERSITY OF MINNESOTA
DOE - $2,490,422; Minnesota U - $2,995,418
10/5/76 - Continuing
Principal Investigator - W. Soderberg

OBJECTIVES – The objective of this coal gasification program at the University of Minnesota Duluth Campus Heating Plant is to demonstrate the cost and environmental effectiveness of converting gas/oil-fired boilers to a coal-derived fuel using a two-stage gasifier. Many institutional, industrial, and commercial boiler plants, such as the University of Minnesota Plant, have been designed for firing only gas and oil and connot be easily converted to coal firing. The two-stage gasifier, when operating at full capacity, will have an anticipated output of 328,882 scf (60°F) of gas with a higher heating value of 166 Btu/scf (60°F). The coal requirement, on maximum load, will be 3t/hr. The two gas streams will have the following cleanup equipment: the bottom gas (1100°F) from the coking section will flow to a refractory-lined cyclone for removal of carryover char particles; the top gas (250°F) from the volatizing section will flow to an electrostatic precipitator for removal of tar oil. After cleanup, the two gases will be combined and piped directly to two water tube boilers. The combined gas will have a temperature of 750°F.

RECENT WORK AND ACCOMPLISHMENTS – Construction work was completed in September 1978 on the gasifier and its auxiliary systems. After approximately 30 days of testing control sequences, stroking of valves and dampers, and calibrating of instruments and meters, the gasifier was fired up, and brought to a stable operating condition using 100 percent coke. The product gas was burned in one of the boilers modified to burn low-Btu gas. Three times an attempt was made to switch from coke to subbituminous coal, and on all three occasions, temperature drop in the top gas required putting the gasifier on hold and starting up again on coke.

PLANS FOR THE COMING YEAR – The gasifier will be down for repairs and modifications for 3 months. Besides opening up the hot gas passages, changes will be made to the ash removal systems and the dust cyclones batch-unloading system. When the system is started up in February, there will be a change in coal–Grass Creek (Wyoming) will replace the Elkol (Wyoming) coal used in the first test. At least five coals will be tested during February, March and April–three Wyoming, one Colorada, and one Indiana–with the one that performs best selected for test during the balance of the year.

PRECOMBUSTION REMOVAL OF SULFUR FROM COAL BY BACTERIAL ACTION

UNIVERSITY OF MINNESOTA
DOE - \$40,000; Minnesota U - \$11,534
9/1/77 - 8/31/79
Principal Investigators - M.R. Hoffmann, H.M. Tsuchiya

OBJECTIVES – The objective of this program is to study microbial processes that will oxidize effectively inorganic and organic fractions of sulfur in coal to water extractable compounds under ambient conditions. Optimal chemical, biochemical, and physical conditions and fundamental kinetic parameters are being determined. New analytical techniques are being applied to the analysis of sulfur in solid coal samples and to the separation and quantification of soluble sulfur species generated during desulfurization. Results of these studies are expected to provide viable alternatives for coal cleaning that can be implemented within a framework of existing technology and to elucidate mechanisms by which microorganisms catalyze the oxidation of metal sulfides, organic sulfides and heterocyclic sulfur compounds.

RECENT WORK AND ACCOMPLISHMENTS – Distinct strains of *Thiobacillus ferrooxidans (T.f.), Thiobacillus thiooxidans (T.t.), and Beijerinckia lactiogenes (B.l.)* were grown in batch reactors under optimal conditions. Coal from mines located in Ohio, Indiana, Alabama, Illinois, and Kentucky was crushed and analyzed for total sulfur content and innoculated with various combinations of bacterial strains in heterogeneous batch reactors. Reduction of the total sulfur content, appearance of soluble sulfur and iron in aqueous solution and pH was monitored as a function of time. Initially, the kinetics of the oxidative dissolution of iron pyrite found in coal was studied as a function of particle size, weight-to-volume ratio, and nutrient concentrations. Under minimal nutrient conditions, the combination of *T.f.* and *T.t.* proved to be the most effective catalyst for the oxidative dissolution of iron pyrite, although in each case nonbiological leaching was a significant factor. After a moderate bacterial lag period of 5 to 10 days, greater than 90 percent of the initial iron pyrite was removed in the subsequent 20 days; however, a pH-dependent precipitation of jarosite was observed in each case. Optimal leaching rates were observed when phosphate concentrations were extremely low. High-phosphate nutrient media had a pronounced inhibitory effect on the dissolution rate. *Beijerinckia lactiogenes*, a nitrogen-fixing bacteria, did not act in mutualism with *T.f.* or *T.t.* nor did its presence enhance the observed rates of dissolution. The rate of oxidative dissolution appears to be independent of decreasing particle size or total surface area when $D_p < 150\mu$. Some coal samples were totally resistant to bacterial leaching even though their pyritic sulfur content was moderately high. The total rate of oxidative dissolution appears to the sum of a chemical rate, an autocatalytic rate, and a bacterial rate. A new technique for total sulfur determination using rapid temperature-programmed pyrolysis at 1400°C has been tested. After pyrolysis, gaseous sulfur compounds are reduced by the hydrogen carrier gas over a Pt catalyst. H_2S produced by this procedure is resolved on a standard chromatographic column using a thermal conductivity detector. Quantification is achieved by using a standard calibration curve. An automated technique for isolating and quantifying soluble sulfur oxyanions by high-speed anion exchange chromatography (ion-chromatography) has been adapted for monitoring sulfur conversions.

PLANS FOR THE COMING YEAR – Kinetic optimization will continue with emphasis on reduction of the bacterial lag phase by adjustment of the culture age and control of the carbon-dioxide concentration. Kinetic studies will shift from batch reactors to continuous-flow systems in which the holding time will become an important variable to be studied. Mechanistic and mathematical models for the overall leaching process will be refined and tested. Experimental conditions that result in minimal jarosite formation will be identified. Bacterial strains isolated from the mining sites under study will be tested and compared to the activity of pure cultures. Bacterial strains capable of degradative oxidation of thiophene derivatives will be isolated from oil-enriched soils by trace enrichment procedures and subsequently tested on coal samples from which iron pyrite has been removed. The mutualistic interaction of *Leptospirillum ferrooxidans* with *T.t.* and *T.f.* will be explored.

PRECOMBUSTION DESULFURIZATION OF COAL

UNIVERSITY OF MINNESOTA
DOE - $233,635; Minnesota U - $13,145
9/16/78 - 9/15/79
Principal Investigators - H.M. Tsuchiya, M.R. Hoffmann

OBJECTIVES – The objective of this program, done in parallel and as an outgrowth of another University of Minnesota contract with DOE, is to study the kinetics and mechanisms of chemical and bacterial leaching of inorganic and organic sulfur compounds present in coal. Optimal chemical, biochemical, and physical conditions for batch, plug-flow, and continuous-flow reactor systems are being determined. Alternative analytical procedures for the analysis of solid sulfur compounds in coal and for the separation and quantification of soluble sulfur species are being investigated. Results of these studies are expected to provide viable alternatives for coal cleaning that can be implemented within a framework of existing technology and to elucidate mechanisms by which microorganisms catalyze the oxidation of metal sulfides, organic sulfides, and heterocyclic sulfur compounds.

RECENT WORK AND ACCOMPLISHMENTS – This work is just getting underway. Initial experiments were focused on a survey of multiple combinations of bacterial strains with different coal samples in batch reactors. An automated technique for isolating and quantifying soluble sulfur oxyanions by high-speed anion-exchange chromatography (ion chromatography) has been adapted for monitoring sulfur conversions. An alternative speciation technique for the sulfur oxyanions using differential pulse polarography (DPP) has been developed. Electron and X-ray diffraction patterns have been used to characterize the solid phases formed during oxidative dissolution of iron pyrite. X-ray fluorescence and electron microprobe spectroscopy has been used to study the distribution of pyrite and other mineral phases in coal. Scanning electron microscopy is being used to determine the mode and extent of attachment of bacteria to coal and pyrite surfaces.

PLANS FOR THE COMING YEAR – Kinetic optimization will continue with emphasis on reduction of the bacterial lag phase by adjustment of the culture age and control of the carbon-dioxide concentration. Kinetic studies will shift from batch reactors to continuous-flow systems in which the holding time will become an important variable to be studied. Mechanistic and mathematical models for the overall leaching process will be refined and tested. Experimental conditions that result in minimal jarosite formation will be identified. Bacterial strains isolated from the mining sites under study will be tested and compared to the activity of pure cultures. Bacterial strains capable of degradative oxidation of thiophene derivatives will be isolated from oil-enriched soils by trace enrichment procedures and subsequently tested on coal samples from which iron pyrite has been removed. The mutualistic interaction of *Leptospirillum ferrooxidans* with *T.t.* and *T.f.* will be explored. The time-dependent relationship of the metastable sulfur oxyanions formed in aqueous solution will be studied with IC and DPP techniques. The role of Fe(II) in the catalytic activation of molecular oxygen in situ will be investigated.

MASS TRANSPORT CHARACTERISTICS OF ZEOLITE CRACKING CATALYSTS

UNIVERSITY OF MISSISSIPPI
DOE - \$235,307; Mississippi U \$30,847
9/30/77 - 9/30/79
Principal Investigator - H.W. Haynes

OBJECTIVES — This program is designed to assess the significance of intracrystalline pore diffusion limitations when processing coal-derived syncrudes over zeolite cracking catalysts. The experimental work involves parallel determinations of mass transport characteristics and catalyst activities using model coal-liquid compounds. A second objective is to test various zeolite catalysts for their ability to crack coal-derived syncrudes to naphtha. Zeolite catalysts possess selectivity and activity characteristics when processing petroleum streams that are much superior to the older amorphous silica-alumina cracking catalysts. Whether these improvements will also be realized in processing coal liquids is debatable. The large, aromatic molecules produced during coal liquefaction might have great difficulty in penetrating the zeolite crystallite. To define and assess the potential mass transport limitations in these systems is a first step towards developing catalysts specifically for refining coal-derived liquids.

RECENT WORK AND ACCOMPLISHMENTS — Studies of the catalytic cracking of n-butylbenzene, indan, tetralin, decalin, and sym-octahydrophenanthrene over zeolite NaY have been completed. Generally speaking, the product distribution from cracking each of these compounds was consistent with that which would be expected from thermal cracking (Rice-Kossiakoff mechanism). Coke deposition on the catalyst surface was surprisingly low considering the high severities employed. The relative cracking/dehydrogenation selectivities were investigated. With tetralin, dehydrogenation is preferred over cracking although significant conversion takes place by both paths. Quite the opposite is observed with decalin in which cracking selectivity is much greater than tetralin. The GC-diffusivity measurements have been limited to n-butane diffusion in zeolite NaY. The method of analysis provides a time domain solution to the system equations for comparison with the experimental response curve; unfortunately, a discrepancy has been observed between the calculated and experimental results that appears to result from inability of the axial dispersion model to describe extra-particle associated mass transfer in beds of small particles at high velocities. For comparison, some experimentation has been conducted over zeolite NaA. These zeolites are very similar chemically, but differ in their structural configuration. Because of the small pore structure of zeolite NaA, it can be reasonably assumed that any catalysis of these large hydrocarbon molecules is initiated at the external crystallite surfaces. For the compounds studied, the activities were higher by a factor of 40 or more over the NaY catalyst suggesting that the seat of activity for octahydrophenanthrene and smaller species is within the zeolite crystallites primarily.

PLANS FOR THE COMING YEAR — Partially saturated molecular species larger than the octahydrophenanthrene will be prepared and purified for use as reactants in the continuing catalytic cracking studies. Other catalysts to be tested include a hydrothermally stabilized NH_4Y zeolite (ultrastable Y) and a chemically dealuminated NH_4Y zeolite. Hydrocracking studies will be underway shortly. At the culmination of the reactor studies, a real coal-derived liquid will be subjected to catalytic cracking, hydrocracking, or both. More experimentation with n-butane diffusion in NaY is planned to identify conditions under which the mathematical model is applicable. The diffusivities of large hydrocarbons in Y-type zeolites will be investigated then.

SMALL-ANGLE X-RAY SCATTERING STUDIES OF COAL SAMPLES POROSITY

UNIVERSITY OF MISSOURI-COLUMBIA
DOE - $94,551
9/30/78 - 9/30/80
Principal Investigator - P.W. Schmidt

OBJECTIVES — Small-angle X-ray scattering, which is a useful and convenient technique for investigating the porosity and other submicroscopic structure of materials, is being used to study the porosity of coal samples obtained from a number of sources. Preliminary data from some coal samples suggest that techniques developed for the porosity of charcoals can be applied to coals. From the scattering data, it is possible to calculate the specific surface and to investigate the pore structure (including the contribution from the micropores) that have dimensions no greater than about 15Å. In addition, the results obtained with charcoals suggest that platelet-like pores can be investigated. The small angle X-ray scattering data will be used to obtain information about: the specific surface and porosity of a series of coal samples, ranging from low to high rank, of anthracite, bituminous, and subbituminous coals and lignite; how the viscosity of synthetic oil produced in some coal liquefaction processes is related to the asphaltene concentration and aging; and the specific surface and porisity of coal macerals.

RECENT WORK AND ACCOMPLISHMENTS — Small-angle X-ray scattering data have been obtained for 10 samples of coal of different ranks and for 6 coal chars. All of these samples were supplied by Pittsburgh Energy Technology Center. The scattering curves are now being measured a second time, usually with a different sample of the same coal or char, to be sure that the data are reproducible and and characteristic of the coal or char. The form of the scattering curves has been found to depend on the coal or char; however, attempts to relate these changes to the submicroscopic structure of the scattering sample will be postponed until all scattering curves have been reproduced.

PLANS FOR THE COMING YEAR — When this analysis of the scattering curves has been completed, the results will be compared with other information about the samples, such as the mineral or ash content. In addition, when possible, the specific surfaces of the coal samples will be calculated from the X-ray scattering curves and compared with specific surface data obtained from BET Adsorption data. Other coal and char samples will be investigated, and the study of synthetic oils will be started.

DIRECT COAL UTILIZATION USING ELECTROCHEMICAL DESULFURIZATION

UNIVERSITY OF MISSOURI - COLUMBIA
DOE - $40,000; Missouri U - $2963
8/1/77 - 7/31/79
Principal Investigator - J. Winnick

OBJECTIVES – An electrochemical cell is being tested as a means for removing and concentrating the sulfur oxides from fuel gases. The flue gas produced from the burning of typical high-sulfur coals contains about 0.3 percent sulfur oxides. Regenerable methods (second-generation) require several steps in the process of attaining marketable acid or elemental sulfur. The electrochemical technique has the potential for one-step continuous operation requiring no reagents, as well as the production of high-quality concentrated (> 100 percent) acid. No sludge is produced, and no gas reheat is required.

RECENT WORK AND ACCOMPLISHMENTS – A laboratory-scale molten-salt electrochemical device has been built. The design is based on successful molten-carbonate fuel cells. Synthetic flue gas passes through the cathode chamber. Low-pressure drops are required since the gas does not pass through the electrolyte. The cell operates at stack temperature, obviating the need for reheat. Concentrated SO_3 has been observed emanating from the anode chamber. The flue gas was found to be desulfurized by more than 90 percent. Electric power is supplied at a rate of about 2 percent of the generated power from the plant, at low (∿1 v) potential. In this mode of operation, it appears the anode electrode must be plated with noble metal in a manner similar to the automobile catalysts.

PLANS FOR THE COMING YEAR – Successful operation has been observed with concentrated SO_3 as the product. It may be even more desirable to have elemental sulfur as the product. In this mode, reducing gas rather than electrical power would be supplied. Since the reducing gas will depolarize the anode, nickel or other non-noble electrode metal can be used. Tests of this mode will be performed.

IMPROVEMENTS ON $LaCrO_3$-BASED MHD ELECTRODES

UNIVERSITY OF MISSOURI - ROLLA
DOE - $25,000; Missouri U - $1316
9/1/78 - 8/31/79
Principal Investigator - H.U. Anderson

OBJECTIVE – The problem of corrosion of spinel second phases in Mg-doped $LaCrO_3$ MHD electrodes has been recently identified. It has been shown that if sufficient quantities of Cr are lost from the electrodes during either fabrication or operation hydrolysis of the free La, there is a serious problem. If $LaCrO_3$-based electodes are to be used successfully in MHD channels, it is essential that the solubility limits of the Mg in the $LaCrO_3$ be established as a function of cation stoichiometry resulting from the fabrication processes. The proposed project addresses these two important problems, and its successful completion would make it possible to fabricate single-phase Mg-doped $LaCrO_3$ electrodes that would not be endangered by hydrolysis.

RECENT WORK AND ACCOMPLISHMENTS – The study has been divided into three tasks; specimen preparation (essentially completed), determination of Mg solubility limits (75 percent complete), and determination of changes in cation stoichiometry resulting from fabrication and vaporization (just starting). Sepcimens of $La_{1-y}(Mg_xCr_{1-x})O_3$ and $La_{1-y}Cr_{1-x}Al_xO_3$ have been prepared both as powders and sintered ceramics. For preferential sublimiation studies, selected specimens have been annealed at 1750°C for up to 48 hr. Oxidation-reduction experiments have been carried out on powder specimens as function of Mg content and cation stoichiometry. X-ray diffraction data have been obtained on all compositions, and the data analysis is nearing completion. Electrical conductivity measurements are being carried out. Specimens are being examined with a metallograph in an effort to determine presence of second phases in the base material. It has been established that the solubility of Mg in $LaCrO_3$ is a function of the A-site-to-B-site ratio ($LaCrO_3 = ABO_3$). As the A/B ratio decreases towards 0.9, the solubility limits significantly decrease. The precise limits have not been established, but they are approximately 8 to 10 m percent Mg for A/B = 1 and 3 to 5 m percent for A/B = 0.9. The existence of a $MgCr_2O_4$ second phase when the solubility limits of Mg_nLaCrO_3 are exceeded has not been confirmed by X-ray diffraction or optical microscopy; however, the oxidation-reduction and hydration data certainly suggest its existence by indicating the presence of excess La and a decreased amount of Mg_n solid solution.

PLANS FOR THE COMING YEAR — The oxidation-reduction and X-ray diffraction will be completed to fix precisely the solubility limits of Mg in $LaCrO_3$. The AES and ESCA analysis will be finished in order to determine changes in stoichiometry resulting from the preferrential loss of Cr from the surface.

THERMAL ANALYSIS OF IN SITU CONVERSION OF COAL

UNIVERSITY OF MISSOURI-ROLLA
DOE - $49,898; Missouri U - $2626
9/1/78 - 8/39/80
Principal Investigator - R.L. Davis

OBJECTIVES — Phase I includes the formulation of a realistic analytical three-dimensional model to be used in the thermal analysis of in situ coal gasification together with the preparation of pre- and post-processing routines for the thermal analysis computer program. Also included is the development of various two-dimensional models (axisymmetric and plane models) that approximate the actual situation.

RECENT WORK AND ACCOMPLISHMENTS — A pre-processing routine is being written to build the three-dimensional mesh required by the thermal analysis main program. The pre-processor uses dimension data on the overburden, coal seam, underlayer, and hole to generate the nodal and element data required. The two-dimensional models are providing approximating results, at a much reduced cost compared to the forthcoming three-dimensional analysis, and these results are helpful in defining the relative significance of the parameters associated with the problem under study.

PLANS FOR THE COMING YEAR — The completion of the pre-processor routine and writing of a post-processor routine will be the first priority. Also, the gathering of information on the in situ gasification process as required to formulate the thermal analysis problem will continue. In particular, more definitive data regarding material properties, burn rates, and combustion temperatures will be acquired and utilized. Trial runs with the three-dimensional program will be initiated, and several additional two-dimensional analyses will be performed.

CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES FOR USE IN GASIFIERS

UNIVERSITY OF MISSOURI - ROLLA
DOE - $181,751
5/1/76 - 4/30/80
Principal Investigator - D.E. Day

OBJECTIVES – This investigation is to provide an understanding of the factors controlling the corrosion resistance of refractory oxides, particularly the bond phases, to the high-pressure-high-temperature gases generated in coal gasifiers.

RECENT WORK AND ACCOMPLISHMENTS – The physical and chemical properties of calcium aluminate cement-bonded (dense high alumina, dense intermediate alumina, and insulating) castables and phosphate-bonded (dense high alumina) ramming mixes were investigated after exposure to the DOE* atmosphere for 60 days and CO-steam (CO/steam ratio - 0.1,1and 3) atmospheres for 20 days at 1000 psia/400 to 1000°F. Tests were performed in unsaturated vapor, saturated vapor, and liquid environments. The effect of temperature, pressure, exposure time, and gas composition on the refractories was evaluated from changes in their chemical composition and physical/mechanical properties. The calcium aluminate cement bond shows the most chemical reaction with both the DOE and CO-steam atmospheres. In all three types of castables, the principal reactions in saturated atmospheres (below 700°F) consist of the cement-bond phases reacting with H_2O(Steam) and CO to form boehmite and $CaCO_3$. In unsaturated atmospheres, only $CaCO_3$ is formed. Similar to earlier results, the formation of boehmite was accompanied by a large increase in the flexural strength of dense alumina castables. There was essentially no major property change between 10 and 60 days; after 60 days, the porosity was essentially the same as that for unexposed samples fired in air at 500°F. This increase is tentatively attributed to the dissolution of CaO from the cement-bond phases. The results for a 20-day exposure in atmospheres of CO/H_2O ratio = 0.1,1, and 3 indicated an increasing dissolution rate of CaO with increasing CO/H_2O in ratio and for samples immersed in liquid (gas-saturated H_2O), compared with those in contact with saturated vapor only. Except for the pure calcium aluminate (SiO_2-free) castables, the dissolution of CaO did not appear to affect the structural integrity of the castables. The presence of SiO_2 in the refractory seems to have beneficial effect on the flexural strength of the castables. In an unsaturated atmosphere, the modulus of rupture of SiO_2-containing high and intermediate alumina castables was either increased or the same as that before exposure. High-purity silica-free alumina castables were somewhat weaker. XRD analysis of these castables does not indicate the formation of any new compound. An investigation was undertaken to evaluate the effect of repeated temperature/pressure cycling upon the mechanical strength the thermal expansion of alumina castables. Initial results show that SiO_2-containing castables retain their strength even after five cycles of boehmite formation/decomposition caused by temperature/pressure cycling. The physical/mechanical properties of phosphate-bonded refractories showed relatively little change except for exposure to saturated atmospheres where a significant reduction in flexural strength occurred. This reduction in strength is attributed to leaching of the phosphate bond phases from the refractories in saturated atmospheres. The presence of 1 vol. percent H_2S in the test atmospheres had no major effect upon refractory properties.

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*DOE atmosphere (Vol. percent): CO = 18, CO_2 = 12, H_2 = 24, CH_4 = 5, and H_2O (steam) = 41 plus 1 vol. percent H_2S.

PLANS FOR THE COMING YEAR – Temperature/pressure cycling effects upon the mechanical and thermal shock properties will be further investigated and correlated with any changes in chemical phases, density, porosity and microstructure. Other tasks are to investigate liquid versus vapor corrosion; determine the dependence of the chemical reactions occurring in dense and insulating alumina castables upon the degree of saturation of the atmosphere and correlate these reactions with the physical and mechanical properties; and determine the time, temperature, and pressure dependence for hydrothermal reactions occurring in commercial calcium aluminate cements investigate the reaction of pure $CaO\text{-}Al_2O_3$, and $CaO\text{-}2Al_2O_3$with hydrothermal atmospheres relevant to coal gasification.

IMPROVED SPARK-IGNITION ENGINE EFFICIENCY THROUGH TURBOSUPERCHARGED LEAN OPERATION

UNIVERSITY OF MISSOURI- ROLLA
DOE - $50,000; Missouri U - $2632
9/1/78 - 8/31/80
Principal Investigator - R.T. Johnson

OBJECTIVES – This research program addresses the problem of improving the efficiency of automobiles by recovering waste energy from the engine exhaust. The use of an exhaust-driven turbocharger with a lean combustion engine will be evaluated. Preliminary data indicate that the lean turbocharged system shows promise of improving engine efficiency without increased emissions. There is some indication that this system could replace the catalytic converter system for the reduction of HC and CO emissions. The program is being conducted in two phases: first, a detailed feasibility study using a supercharged single-cylinder research engine intended to determine relationships between emissions, fuel economy, and available exhaust energy for lean supercharged operation; second, single-cylinder engine study results will guide a thorough examination of the emissions and fuel economy characteristics of a lean turbocharged multicylinder engine. An engine dynamometer study, including some transient testing, is planned.

RECENT WORK AND ACCOMPLISHMENTS – All work performed has been preliminary in nature. A short test program using a carburetted single-cylinder research engine that was lightly supercharged has been completed. This program demonstrated the possibilities of reduced NO_x, HC, and CO emissions with increases in efficiency for fixed power levels. The program also demonstrated the difficulties anticipated in supercharging a carburetted single-cylinder engine. Fuel injection equipment and appropriate instrumentation are now on order, and detailed planning and literature reviews are underway.

PLANS FOR THE COMING YEAR – An extensive single cylinder engine study will be conducted with the objectives being to characterize the operation of the lean supercharged engine relative to a naturally aspirated engine. Data will be gathered to characterize emissions, fuel economy, and available exhaust energy for the naturally aspirated and supercharged engine. This information will be the basis for the program dealing with lean supercharged operation of a multicylinder engine. Major planning and logistics efforts for the multicylinder, turbosupercharged engine program will be undertaken during the summer and fall of 1979.

DEVELOPMENT OF LONGWALL WATER-JET MINING MACHINE

UNIVERSITY OF MISSOURI-ROLLA
DOE - $704,158; Missouri U - $37,031
5/7/75 - 12/31/78
Principal Investigators - D. Summers, C.R. Barker

OBJECTIVES — This work involves R&D into the application of a series of high-pressure (69 MPa) water jets to a mining machine for use in longwall coal mining.

RECENT WORK AND ACCOMPLISHMENTS — Earlier, an experimental cutting head had been built and field tested in a surface coal mine. Several potential advantages to the use of this unit, including potential higher productivity and the elimination of coal dust and gas ignition hazards, led to the design and construction of a preliminary prototype for further testing This head, built around the requirements necessary to test shearers and other existing mining equipment, was taken to the artificial coal surface test facility at Bruceton, Pennsylvania. Preliminary tests showed that the artificial coal did not adequately simulate coal in response to water-jet attack. Thus, activity has been directed toward finding an acceptable artificial material. The trials were at laboratory scale, so that the results can be held to be only provisional; nevertheless, a mix was created that adequately simulated the response of coal to jet attack.

PLANS FOR THE COMING YEAR — The contract will be completed soon; however, a proposal has been submitted to extend the project to permit completion of the surface testing of the new cutting head and evaluating its potential performance.

MECHANISMS AND RATE OF ALKALI TRANSPORT IN COAL GASIFICATION PROCESSES

UNIVERSITY OF MISSOURI-ROLLA
DOE - $153,727; Missouri U - $30,265
9/76 - 3/79
Principal Investigator - G. Lewis

OBJECTIVES — The objective is to evaluate and assess the degree and significance of alkali vaporization and transport under the temperature, pressure, and atmospheric conditions characteristic of various coal gasification processes. The work will involve both calculated relations and experimental confirmation.

RECENT WORK AND ACCOMPLISHMENTS — The thermodynamic stability of the alkali-oxides, sulfates, nitrates, carbonates, sulfides, cyanides, and selected silicates at various temperatures, pressures, and atmosphere compositions (assumed to exist in high- and low-Btu gasifiers) have been evaluated. The extensive calculations are being reworked into a graphical form to make relations involving significant alkali transport easily identified and compared to other reactions. Thermal analysis (weight loss) experiments using the "ERDA atmosphere" have been made on selected alkali compounds in a Mettler thermoalalyzer. Significant modifications to the apparatus have been made to allow operation under reducing conditions. The experiments are limited by severe deterioration of the fused-silica Mettler furnace after alkali transport has been observed. A thermal transport furnace system (operated at atmospheric pressure) has been constructed to avoid these materials problems and 35 runs have been completed, comprising samples of K_2SO_4,Na_2SO_4, and Ohio-10 coal ash, as well as sample-less runs for background determinations. The atmosphere used has been water-saturated DOE atmosphere. The water partial pressure has been far less than the approximately 50 percent level established for the high-pressure runs. A high-pressure thermal transport furnace system has also been constructed and tested, with 32 runs completed. Samples of K_2SO_4 and Ohio^{-10} coal ash, as well as samples runs for background determinations, have been run at 50, 100, 250, 500, and 1000 psig. The vaporization of K_2SO_4 appears to be consistent with congruent behavior; that is, vaporization products are formed of the same gross composition as the condensed phase. The data from a typical run on Ohio^{-10} coal ash appear to have a very high initial alkali loss rate. After a few hours time the alkali loss rate decreases to a value essentially consistent with the system background rate. This behavior could be explained by forming a concentration gradient in the sample as proposed in glass samples investigated by Wenzel.* In a coal gasifier where the ash bed could be very active and hence the formation of concentration gradients suppressed, the data imply that very high alkali transport rates could be observed. The transport of sulfur compounds has been followed via pH changes in the condensed water extracted from the gas flow after the high-temperature reactor. It has been observed that minor amounts of the alkaline earths, calcium and magnesium, are transported along with the alkalis. Data on the effect of increased system pressure on the vaporization behavior of K_2SO_4 appear to indicate that the vaporization rate decreases as pressure increases; however, it should be noted that the composition of the condensed sample is changing with pressure. These observations suggest at least two mechanisms leading to suppressed vaporization of alkali: one may not be pressure induced (that is the formation of a concentration gradient in the sample); the second appears to be pressure related (that is, the formation of new phases at high pressures that have much lower alkali vaporization rates).

PLANS FOR THE COMING YEAR — This project is presently scheduled to be terminated by April 1979.

CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS

MONTANA STATE UNIVERSITY, BOZEMAN
DOE - \$205,932; Montana SU - \$37,031
6/20/75 - 6/19/79
Principal Investigators - L. Berg, F.P. McCandless

OBJECTIVES — The program is seeking to develop processes to convert liquefied coal into clean distillate fuels. It is limited to research on liquefied coal made by the COED, SRC, Synthoil and H-Coal processes, all of which have reached the pilot plant scale. This work will be accomplished by the use of either existing or new hydrotreating catalysts for the hydrocracking of the liquefied coal at conditions of temperature, pressure, residence time, and hydrogen flow rate that are relatively moderate. If coal is ever to replace petroleum, in part, as a source of motor, diesel, jet, and/or burner fuel, it is essential that the product from current coal liquefaction processes be modified and upgraded to suit modern combustion engines at lowest costs.

RECENT WORK AND ACCOMPLISHMENTS — COED pyrolysis oil was hydrotreated in both batch and continuous trickle flow reactors at 415°C, 800 psig, and hydrogen flow rate of 10,000 scf/bbl. The best commercial catalysts found for nitrogen removal were the nickel molybdates, specifically Shell 324, Cyanamid HDS-9A, and Harshaw HT-500; the best for sulfur removal are Harshaw HT-400, Shell 344, and Cyanamid HDS-20A, all cobalt molybdates. An improved catalyst for heteroatom removal fabricated here is a cobalt-nickel-molybdate of large surface area and pore volume. The catalytic hydroteating of Synthoil at 415° to 450°C, 800 psig, LHSV of 1.0 and

H_2:oil ratio of 10,000 scf/bbl showed Shell 324 nickel molybdate to be the best for nitrogen removal, about 43 percent. The best sulfur removal, about 70 percent, was obtained with a cobalt-nickel-molybdate on large surface area and pore volume base fabricated here. In the catalytic hydrotreating of SRC at 450°C, 800 psig, 10,000 scf of H_2/bbl, and LHSV of 0.5 to 1.5, the best commercial catalyst for nitrogen removal is Harshaw HT-400 cobalt molybdate. Cyanamid HDS-20A cobalt molybdate gave the best sulfur removal of the commercial catalysts tested. Somewhat better nitrogen and sulfur removal from SRC-II was obtained with an MSU high-surface-area large-pore-volume nickel-cobalt-molybdate. After evaluating more than 50 commercial catalysts, it has been shown that at moderate processing conditions, none of them are especially effective in removing the heteroatoms from coal liquids and tha nitrogen removal is the most difficult. An improvement in heteroatom removal over commercially available catalysts was obtained when a nickel-cobalt-molybdate catalyst is prepared on an alumina base containing high surface area and large pore volume.

PLANS FOR THE COMING YEAR – Heteroatom removal from SRC-II will be investigated by means of combinations of nickel. cobalt, molybdenum, and tungsten on alumina-base materials characterized by high surface area plus large pore volumes. Several catalyst base materials having different and specific pore volumes, pore diameters, and surface areas have been secured. They will be impregnated with the metals active as hydrotreating agents and evaluated in batch and continuous hydrogenation reactors. It is anticipated that the properties of the base materials will cause a significant difference in their hydrotreating capability.

DIRECT CONVERSION OF LIGNITE TO CHEMICAL FEEDSTOCKS

MONTANA STATE UNIVERSITY
DOE - $19,135
12/21/77 - 12/20/78
Principal Investigator - W.P. Scarrah

OBJECTIVES – This program seeks to: determine the potential for directly converting lignite to chemical feedstocks via a process combining technologies from molten salt catalysis and solvent refining; investigate the effects of alkali metal halides added to zinc chloride catalyst on product distribution and hydrocarbons-salt separation; determine the effects on product distribution of hydrogen sources as influenced by reducing gas composition, lignite moisture, and added water; and identify the significant processing variables (alkali metal halides and hydrogen sources) preparatory to more comprehensive process studies.

RECENT WORK AND ACCOMPLISHMENTS – Experimental batch runs (450°C, 3000 psig, 15 min.) in a rocking autoclave have been completed. The interactions between zinc chloride catalyst alkali metals (lithium, sodium, or potassium) and halides (chlorides, bromides, or iodides) were investigated using a randomized complete block experimental design. The effects on product yields of halides, reducing gases (hydrogen, carbon monoxide Syngas), and water sources (wet lignite, dry lignite, dry lignite plus added water) were evaluated using fractional factorial experimental designs. Products were characterized using a modification of sequential elution with specific solvents chromatography (SESC)—a technique developed by Mobil to separate products relative to their chemical functionality. The product yields determined were oils, asphaltenes (monofunctional compounds), and asphaltols (multifunctional compounds primarily resulting from -OH groups).

Preliminary data analysis indicates the yields of all products are less when using lithium than sodium and potassium. The halides significantly affect yields with the bromide being preferred for sodium and the iodide for potassium. Carbon monoxide significantly decreases yields; Syngas improves yields with sodium and either Syngas or hydrogen works well with potassium. Dry lignite plus added water increases yields for both sodium and potassium; dry lignite particularly reduces yields when using potassium.

PLANS FOR THE COMING YEAR – This contract will end soon; however, the data will still be undergoing analysis, and the final report will be in preparation. Because of the unexpected and promising results of this experimental work, comparisons will also be made with previous work to determine the most promising conditions for more comprehensive process studies.

METHODS AND COSTS OF THIN SEAM MINING

MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY
DOE - $46,868; Montana Tech - $4318
9/25/77 - 12/24/78
Principal Investigator - T.E. Finch

OBJECTIVES – Thin seam mining methods will be examined at surface coal mines in the Western United States and the associated costs of such methods ascertained. Thin seam coal mining in the Western United States normally equates to recovery of stray seams associated with thicker, major seams. The thin or stray seams encountered are generally recovered, but not in all cases. The alternative to extraction, of course, is spoiling. Operationally, stray seams create irritating scheduling problems and require special handling techniques that do not always lead to efficient equipment utilization. Additionally, coal recovery from a thin seam is considerably less than the 95 percent usually recovered from thick seams. Higher recovery in thin seams leads to dilution problems that depreciate Btu quality, and most Western coals are not in a position to lose heating value. Thin Western seams also undulate and pinch or swell more than thick seams, which leads to more difficult recovery. Often they are associated with equally dark carbonaceous shales, and visual selectivity is difficult at best during daylight hours. Surface mine operators with thin or stray seams have addressed their presence in various manners: they ignore the resource and spoil the coal; some recover thin seams as convenience allows; and others have established methods of thin seam recovery. A thin seam is always a resource, but economics often refute their existence as a viable reserve entity. Trends by Federal and state regulatory agencies imply that stray seams will require economic justification if they are to be spoiled.

RECENT WORK AND ACCOMPLISHMENTS – The project is almost completed; a final draft report is nearly ready for review by DOE. The results are reported as unit operations that examine: thin seam extraction and its effects and added costs on overburden handling; conventional thin seam extractive methods; and new or proposed methods of thin seam removal. Included within the report is a review of state and Federal regulations and philosophies covering stray seam recovery. Another section reviews existing Western surface mines that mine thin seams. The value of this type of examination is twofold: it serves as a guide for mine planning for private industry; and it offers guidelines for Federal and state agencies contemplating resource recovery regulations or resource evaluation. In these times of inflationary regulatory concern, the costs projected differentiate true reserves from measured resources.

PLANS FOR THE COMING YEAR – The project will be completed early in the coming year.

ENVIRONMENTAL EFFECTS FROM LEACHING OF COAL CONVERSION BYPRODUCTS

UNIVERSITY OF MONTANA
DOE - \$74,948; Montana U - \$17,400
6/75 - 6/78
Principal Investigators - W.P. Van Meter, R.E. Erickson

OBJECTIVES — Most of the trace mineral content of coal will remain with the solid residues or byproducts of a gasification facility. Surface landfill or strip-mine backfill are among the more obvious disposal options for this material, either of which would subject it to probably percolation or infusion by precipitation or groundwater. This project will study solid by products from existing pilot of full-scale facilities by column leaching methods with the purpose of determining whether potentially hazardous amounts of toxic elements may be leached into ground or surface water. This information will provide a basis for decisions concerning the ultimate disposal of wastes.

RECENT WORK AND ACCOMPLISHMENTS — The experimental work of this project has been completed, and a final report will be available soon. During the project specimens were received from the following facilities: AN - South Africa (a Lurgi process); CO - COGAS(COED), Leatherhead, England; IG - HYGAS, Chicago; MO - ERDA-MERC, Morgantown; RC - CO-2 Acceptor, Rapid City; SY - Synthane, Pittsburgh; and WE - Westinghouse PDU, Pittsburgh. These materials have been examined by a column leaching procedure using distilled water, 0.01 N H_2SO_4, 1.0 M ammonium acetate, and natural groundwater obtained from wells near Colstrip, Montana. The effluents have been analyzed for Na, K, Mg, Ca, Sr, Mn, Ni, Cd, Hg, Pb, and F; except for the F (specific ion electrode), all analyses were by atomic absorption spectrometry. The results of the studies indicate that there is only minor potential for harmful pollution of water systems by any of the more toxic heavy metals listed. Some of the residues tested release large amounts of alkali (as lime). The data have been organized for presentation in two forms: statements of the total amount leached in parts per million (micrograms leached per gram of material), and listings of the peak concentration observed in the column effluent. The latter is informative in a relative sense, but subject to temperature and flow rate. In all cases the columns were at ambient laboratory temperature, made of Pyrex glass, 27mm inside diameter, and the flow rates were about 7 milliliters/hr.

Full data on total amounts leached per unit mass, and maximum concentrations observed are given in the final report for each of the specimens received under the effect of each of the eluant liquids. Elution curves are presented in the report for about 20 percent of all the column runs made.

PLANS FOR THE COMING YEAR — This project has been completed.

FOSSIL 1: DYNAMIC SIMULATION MODEL OF U.S. FOSSIL ENERGY TRANSITION, 1975-2020

DARTMOUTH COLLEGE
DOE - \$449,790
1/26/76 - 3/30/79
Principal Investigator - D.L. Meadows, G.A. Backus

OBJECTIVES — A long-term policy analysis tool is being developed to determine the effects of a national energy policy RD&D, world oil prices, and economic growth on the market penetration potential of new energy technologies.

RECENT WORK AND ACCOMPLISHMENTS – Focus has been on the development of a major disaggregated computer model of the U.S. energy system. The preliminary model, FOSSIL 1, was completed and documented in 1977. The model subsequently received an independent review by Pugh Roberts Associates, Inc., of Cambridge, Massachusetts from which many potential enhancements were realized. The enhancement, validation, and documentation of the resulting model, FOSSIL 79, were the major tasks here. The original FOSSIL 1 model, used by over 150 companies and universities, including the EPRI-sponsored Energy Modeling Forum for studying the future supply of coal and the response of consumers to rising energy prices. The new model is also being used by the Energy Modeling Forum for domestic oil and gas supply studies, and by DOE's Office of Policy and Evaluation for analysis of the next National Energy Plan. FOSSIL 79 is a system dynamics model which simulates the U.S. energy system over the years 1950-2020. It uses an interactive set of differential equations, is user-oriented, and permits easy alteration of key variables for policy testing. Energy supply is modeled through 39 production types–2 for coal, 8 for gas, 6 for oil, 14 for electricity, and 1 for solar-geothermal heating. Demand for energy is broken into two parts. End-use demands are a function of energy price and availability and an exogenously supplied GNP. Secondary demands for primary fuels by electricity and synthetic fuels are explicitly included. OPEC import prices and supply are exogenously determined in FOSSIL 79. Maximization of supply/demand interactions is not an input assumption, although the energy market in FOSSIL 79 attempts to reach its natural equilibrium. Forces that constrain the path to equilibrium –construction delays, price regulation, and imperfect knowledge–are endogenous to the model. The model uses reasonable expectations to endogenously simulate investment decisions. It contains detailed financial subsectors that allow implicit implementation of regulation and tax policies. Further, a financial subsector can determine the aggregate balance sheet for any energy industry in any given year. Production subsectors explicitly consider the processes and cost associated with discovery, development, and production. Results generated by FOSSIL 79 indicate a tumultuous energy transition period in the early 1990's. The model result indicates that the current leveling of all domestic oil and gas production will be followed by rather sharp declines in production beginning in the early 1990's. This process, along with the continued growth in U.S. energy demand, could cause major upsets in the world oil market, with resulting high energy prices and extensive acceleration of synthetic fuel programs.

PLANS FOR THE COMING YEAR – Work in 1979 includes the formal documentation of the FOSSIL 79 model. When the documentation reports are completed, this project will formally end; however, a new contract has been initiated that will focus on the interactions of the energy system with the U.S. economy. This study is expected to last 3 years and will build upon the results of the study reported here.

STUDY OF FLY-ASH FORMATION MECHANISM

UNIVERSITY OF NEW HAMPSHIRE
DOE - $223,740; New Hampshire U - $4292
2/76 - 2/80
Principal Investigator - G.D. Ulrich

OBJECTIVES – Recent studies of fly-ash emitted from stationary combustion equipment suggest that substantial numbers of sub-micron particles are discharged even from units having control devices. This fraction is the size least efficiently collected and most damaging physiologically. With the prominence of coal as a fuel, pollution from sub-micron fly-ash particles is receiving increasing attention. Work in this laboratory falls within two categories: The first is a fundamental investigation of collision rates, sticking coefficient, aggregate morphology, fusion rate, and other phenomena that influence the formation and growth of pure and mixed metal oxide particles. This study is being conducted with the aid of a precision laboratory burner. The second category, involving growth ash particles in a full-scale commercial utility boiler, is an effort to determine fly-ash characteristics as a function of temperature and residence time in the boiler. Two cyclone-fired units at a nearby power plant have been made accessible for this work. With results from the fundamental study, a model will be formulated to describe particle behavior in commercial boilers.

RECENT WORK AND ACCOMPLISHMENTS – Laboratory flame data, equilibrium predictions, and an ash vaporization mechanism have been used to generate primitive predictions for the size, quantity, and composition of condensation ash in cyclone and pulverized-fuel fired boilers. They agree reasonably well with the size, morphology, and concentration of ash samples extracted from actual boilers. Depletion of aluminum and enrichment of silicon and iron were predicted in the sub-micron ash fraction. These trends were documented for aluminum and silicon, but the actual behavior of iron was contrary to predictions. The growth model was refined further with completion of a computer code that predicts primary-particle and aggregate growth. It encompasses a broad range of conditions in the free-molecule, transition, and continuum regimes of Brownian motion.

PLANS FOR THE COMING YEAR – Refinement and documentation of the ash formation model will continue with the laboratory investigation of flames containing titania, alumina, and alumina-silica mixtures. A series of sample sets taken from various residence times in cyclone-fired boilers will be obtained, analyzed, and employed to test the model.

CATALYTIC COMBUSTION OF COAL-DERIVED GASES

PRINCETON UNIVERSITY
DOE - $124,140; Princeton U - $8580
9/15/77 - 9/14/79
Principal Investigator - F.V. Bracco

OBJECTIVES – The objective is to determine under what conditions coal-derived low- and medium-Btu gases should be burned in a single-stage catalytic combustor to minimize emissions of NO and NH_3 arising from the NH_3 impurity in the fuel. The program involves both experimental and theoretical work. The dependence of catalyst substrate temperature, exhaust gas temperature, and composition on inlet conditions will be determined experimentally. The data will be interpreted using a two-dimensional numerical model for combustion in catalytic pipes. The model will be tested and improved by comparison with the experimental results and, when perfected, will be available for parametric studies, which are difficult to perform experimentally on so complex a system.

RECENT WORK AND ACCOMPLISHMENTS – An experimental study was done on the catalytic combustion of CO, one of the three main fuel constituents of low- and medium-Btu gases. Substrate temperatures, exhaust temperatures, and exhaust compositons were measured for different inlet velocities and CO concentrations. The following observations were made: substrate temperature is only weakly dependent on inlet gas velocity, a relative maximum or shoulder appears in the substrate temperature profile near the inlet, and the disappearance rate of unburned CO in the exhaust is consistent with the homogeneous reaction rate observed in noncatalytic systems. Thus, the exhaust reaction is not catalyzed by species generated by the catalyst.

A numerical model for combustion in catalytic channels has been developed which includes axial and radial heat, mass, momentum transfer, and homogeneous chemical reactions. The wall reactions are assumed to be very fast, and the wall temperature is set equal to the experimentally observed substrate temperature. The predicted conversion of CO is greater than the observed conversion.

PLANS FOR THE COMING YEAR – The planned work includes catalytic combustion of a synthetic coal-derived gas with measurement of substrate temperature, exhaust temperature, and exhaust composition at various inlet conditions. Similar experiments will be done on fuel doped with H_2S to determine if this impurity affects the combustor performance in the regime tested. Also, the fuel will be doped with NH_3 to determine the fraction of NH_3 converted to NO. The feasibility of using resonance absorption to measure species concentrations in the gas will be studied.

MEASUREMENT AND CORRELATIONS OF CONDITIONS FOR RESIDUAL OIL ENTRAPMENT AND MOBILIZATION

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY
DOE - $129,808; N.M. Petroleum Recovery Research Center - $129,808
9/1/78 - 9/1/80
Principal Investigator - N.R. Morrow

OBJECTIVES – The entrapment and displacement of residual oil remaining after waterflood is being investigated in order to test and develop correlations that can be used to predict displacement behavior. These correlations will be applied to measurement of residual oil saturations by near-wellbore techniques and to the tertiary recovery of oil.

RECENT WORK AND ACCOMPLISHMENTS – Work has been done on equipment design and layout, and equipment has been ordered. Core flooding tests will be conducted using positive-displacement pumps when constant flow rates are needed. Flooding at constant pressure will be effected by use of bladder accumulators.

PLANS FOR THE COMING YEAR – An apparatus for displacement of residual oil saturations from reservoir core samples will be developed. The effect of interfacial tension on displacement will be investigated over a wide range of interfacial tensions. A study will be made of the effect of interface velocity on contact angles observed at rough surfaces, and results will be related to previous observations of rate of displacement by imbibition. The entrapment and displacement of single blobs of fluid under well-defined wetting conditions will be used to test a theory of wettability effects. A systematic study will be made of the effect of viscous and bouyancy forces on residual saturations in geometrically scaled porous media. The structure of residual oil in rocks will be investigated by displacement of an oil phase that will solidify. After chemical removal of the rock, the capillary structures formed by the solidified residual phase will be studied in detail. A survey of available methods of determining residual oil saturations in flooded-out reservoirs will be prepared.

ENHANCED OIL RECOVERY BY CO_2 FOAM FLOODING

NEW MEXICO STATE UNIVERSITY
DOE - $300,973; New Mexico State U - $322,712
8/31/78 - 8/30/81
Principal Investigator - J. Patton

OBJECTIVES — This project will develop a commercially feasible oil recovery process in which significant quantities of unrecoverable oil are displaced from the reservoir by injecting CO_2 foam. Commercial surfactants and polymers are being studied to identify the optimum chemical structure and concentrations of these foam generation and stabilizing additives. The objectives of this project include developing a CO_2 foam stable under oil reservoir conditions, determining the rheology of the foam, forming the foam in situ, displacing oil from cores by foam, and describing the process with respect to conformance and efficiency in oil displacement.

RECENT WORK AND ACCOMPLISHMENTS — Since the initiation of the foam stability study on November 1, 1978, 96 surfactants have been evaluated. The evaluation criteria include compatibility with brine and water hardness, ease in foam generation, and foam stability. Particular emphasis has been placed on the effect of temperature (70° to 140°F) on foam stability and the effect of additive concentration ranging from 0.1 to 1 percent. Anionics, which are classified as surfactants, appear superior; however, several nonionics are competitive. Preliminary data suggest some degree of synergism. The optimum foam formulation may contain two or more surfactants.

Preliminary work done on the effect of polymers on the foam stability showed modified cellulosics and xanthan, a biopolymer, as having the most promise. Brine tolerance and thermal stability appear to be responsible for superiority of these polymers. In these tests, various concentrations of polymers were added to brine containing 0.5 wt percent Equex AEM, a Proctor and Gamble surfactant. A broad optimum exists at polymer concentrations between 0.1 and 0.2 wt percent. Foams containing more or less polymers were consistently less stable than those in the optimum range. Preliminary work measuring the viscosity of foams has begun. Many problems have been encountered, and no quantitative results have been obtained.

PLANS FOR THE COMING YEAR — The work on foam stability will continue with the extension of temperature dependence and with the expansion of the effect of polymers. Also, work will be initiated to evaluate the effect of crude oil on the more stable foams. The best formulations will then be subjected to linear flow tests in cores and sand packs. The rheology of the more stable foams will be studied. A tube flow viscometer will be used to correlate results obtained in flow-through packed beds of fine sand. Degradation studies will be made with the surfactant and polymers under typical reservoir conditions and in the presence of high-pressure CO_2.

COAL/WATER/OIL EMULSIONS AS CLEAN LIQUID FUEL

ADELPHI UNIVERSITY
DOE - $198,024; Adelphi U - $19,666
6/7/76 - 8/31/78
Principal Investigator - J. Dooher

OBJECTIVES — This program is investigating the properties of coal/water/oil emulsions including stability, viscosity and combustion characteristics with and without the addition of additives to remove sulfur dioxide.

RECENT WORK AND ACCOMPLISHMENTS – Adelphi Research Center has completed a series of handling and combustion studies on coal/water/oil emulsions, with important progress in both areas. To assess the handling of these mixtures, a pendulum-settling apparatus was refined to permit screening of many different mixtures. This device allows a large amount of data to be taken on the shift in the center of mass of a sample of coal/oil mixtures, including coal/oil/water emulsions. The results of these studies on many different samples indicated that, especially for the light oils, the addition of water aided stability. The dynamic stability of these mixtures was exmained for various shear rates with a concentric cylinder viscometer and a modification of an extrusion rheometer, which tested pipe flow conditions. These data were correlated with the various physical and chemical properties of several different coal samples. The maceral content of the coal was correlated strongly with the viscosity of coal/water/oil emulsions. It is also possible to relate viscosity data to the important parameters of pipe flow such as pressure drop. Results of the combustion studies indicate that similar thermal efficiencies were obtained with coal/water/oil emulsions as with oil. The addition of additives, such as soda ash, has been shown to be very effective in removing sulfur dioxide emissions from the stack gases.

PLANS FOR THE COMING YEAR – This project is being continued on a larger scale to heat and air condition 20 percent of the Adelphi University Campus. Pollutants will be carefully monitored for the effect of fuel additives in removing sulfur dioxide gases.

IMPROVED TECHNIQUES FOR GASIFYING COAL

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK
DOE - $860,000; CCNY - $349,000
6/30/76 - 6/29/79
Principal Investigator - R.A. Graff, J. Yerushalmi

OBJECTIVES – This program intends to lay the groundwork for development by industry of new techniques for converting coal into gaseous and liquid products. The program explores the features and operating characteristics of beds of fine solids fluidized at high velocities, the flash heating of raw coals in gases containing hydrogen at elevated pressures with control of residence time of the vapor, and the flash heating of raw coals in steam at elevated pressure.

RECENT WORK AND ACCOMPLISHMENTS – This program is divided into three research areas: high-velocity fluidized beds, flash hydrogenation, and flash hydrolysis.

High-Velocity Fluidized Beds – The results of experiments conducted with several solids in cold-model equipment have delineated the various vertical gas-solid flow regimes and the transition between them. As the velocity of the gas flowing across a bubbling fluidized bed is raised, the heterogeneous, two-phase character of the bed peaks and then gradually changes, giving way to increasing uniformity culminating in the turbulent state in which large bubbles or voids are absent. In the turbulent fluid bed, an upper level is present though it is more diffused than that of a bubbling bed owing to greater rates of particle carryover. The turbulent regime extends to the transport velocity beyond which solids fed to the bottom of the vessel traverse it in transport flow, and the concentration of the resulting suspension depends not only on the velocity of the gas but on the solid rate. The transport velocity divides the vertical gas-solid flow regimes into stationary states, including the bubbling and turbulent fluidized beds which experience no net flow, except for some carryover, and the transport regime, which encompasses a wide range of conditions from dilute-phase flow to the fast-bed condition. Also, experiments have been conducted to study several practical aspects of the design and operation of a fast-fluidized bed. These aspects include the cyclone system, the standpipe, and the solid-transfer line connecting the standpipe and the fast bed. Understanding the various flow regimes and the transitions between them is essential for choosing and designing a fluid bed system for a given set of objectives. These studies assure the successful development of gasifier systems of advanced design.

Flash Hydrogenation — A comparative study of the flash hydrogenation of nine coals has been carried out. These coals were chosen to represent the U.S. spectrum from lignite through HVAB. While the behavior of these coals was similar, liquid yields varied indicating that liquid yield increases with rank. Two eastern HVA coals gave total liquid yields in excess of 35 percent carbon conversion to liquid product. These results greatly improve the prospects for commercial production of liquids by flash hydrogenation and suggest that yields of single-ring aromatics in excess of 20 percent can be obtained in 100 atm of hydrogen if vapor-residence times beyond 0.6 sec are employed. These results also show that selected coals can provide particularly high-liquid yields in this process. In addition to SNG and light aromatic liquids, flash hydrogenation yields a residual char of substantially reduced sulfur and nitrogen content. Using a bituminous coal containing 6.6 percent MAF sulfur and 1.4 percent MAF nitrogen, chars assaying as low as 1.6 percent MAF sulfur and 0.6 percent MAF nitrogen were obtained in 10 sec with 100 atm of hydrogen pressure. Based on heating values, this amounts to the removal of 76 percent of the sulfur and 51 percent of the nitrogen. The greatly reduced sulfur and nitrogen content of the residual char in flash hydrogenation makes this product more attractive than the feed coal as a boiler fuel. The value added can be estimated as the cost of scrubbing an equivalent amount of sulfur from the stackgases of a boiler plus the cost of an equivalent reduction in NO_x emission. Consideration of the increased value of the char product will improve the economic attractiveness of flash hydrogenation for the production of clean fuels and chemicals. Titanium hydride has been found to promote increased yields of liquids in the flash hydrogenation of coal. The effect begins at about 800°C and increases with decreasing temperature. At 710°C in 100 atm of hydrogen, the yield of liquid heavier than xylene increased from 30 percent in the absence of a catalyst to 60 percent with titanium hydride. This increased liquid yield was at the expense of the less valuable char residue. The yield of other valuable compounds was not reduced. These experiments open the way to the use of catalysts in flash hydrogenation.

Flash Hydrolysis — Flash hydrolysis, the rapid heating of raw coal in steam at elevated pressures, provides high yields of liquids. In 50 atm of steam, up to 45 percent of the coal's carbon is converted to liquid product. These experiments, which were conducted in a bench-scale reactor, provide the basis for pilot-scale work on an alternative process for producing liquids from coal.

PLANS FOR THE COMING YEAR — Work on high-velocity fluidized beds will primarily focus on the study of solid mixing in a bed maintained at gas velocities spanning the bubbling, turbulent, and fast-bed regimes.

Studies on flash hydrogenation will continue with emphasis on the effect of pressure on product distribution, the analysis of liquids, product distribution in CO-H_2 mixtures, determination of char sulfur and nitrogen, and commercial flash hydrogenation reactor design.

Flash hydrolysis yields will be determined in steam, steam-hydrogen mixtures, and steam--carbon monoxide mixtures. Techniques will be developed for the analysis of the liquid product.

HIGH-TEMPERATURE CONDENSATION OF COAL COMBUSTION PRODUCTS

CLARKSON COLLEGE OF TECHNOLOGY
DOE - $97,370; CCT - $9737
9/1/78 - 8/31/80
Principal Investigator - J.L. Katz

OBJECTIVES — Slag vaporization is a serious problem in high-temperature coal combustion and gasification processes. Subsequent cooling of process gas streams causes the slag vapors to condense, but not necessarily at equilibrium. Although the equilibrium properties of coal slags have been studied, little is known about the kinetics of the condensation processes. This project will study the condensation of two important slag constituents: sodium oxide and silica. The vaporization and subsequent condensation of sodium and related compounds can pose problems at normal gasification temperatures. Silica is important at temperatures found in coal combustion.

RECENT WORK AND ACCOMPLISHMENTS — Because funding for this project began September 1, 1978, little work could be accomplished by October 1, 1978. A research assistant was recruited to help with the experiments, and work was begun on the fabrication of equipment.

PLANS FOR THE COMING YEAR — All equipment will be fabricated, and the experiments testing the apparatus will be completed. Preliminary results on one or both of the systems to be studied will be obtained.

SIMPLEX COAL AND BIOMASS GASIFICATION PROCESS

COLUMBIA UNIVERSITY
DOE - $378,000
9/30/77 - 9/29/79
Principal Investigators - H.W. Schulz, J.L. Spencer

OBJECTIVES — This program seeks to develop a coal gasification process that will produce a clean fuel gas cost competitive with the current price of imported oil. The Simplex process provides an efficient means of gasifying the highly caking Eastern bituminous coals in a moving-burden gasifier and a method for converting municipal solid waste (MSW), dewatered sewage sludge (DSS), or shredded forest pulp into a clean-burning fuel or synthesis gas with a heating value of 330 to 440 Btu/scf.

The research phase of this investigation (Phase I), funded by the National Science Foundation, provided a demonstration of proof of principle and the optimization of briquette formulation and fabrication parameters. The process development work (Phase II), funded by the Department of

Energy's Fossil Energy Program is currently in progress and will be completed in the summer of 1979. This phase provides for the experimental optimization of the process variables in the 2-t/d bench-scale slagging gasifier of the Fossil Energy Laboratory at Columbia University. It also comprises the development of a commercial briquetting process employing a high-speed rotary press. Phase III calls for the pilot plant demonstration of the fully developed process in the 25-t/d gasifier of the Grand Forks Energy Technology Center. It is projected that this pilot demonstration will be performed in the fall of 1979.

RECENT WORK AND ACCOMPLISHMENTS – The Simplex project has reached the stage of pilot plant demonstration. A key requirement of the process was to prepare the burden in the form of sturdy briquettes at low cost. The cellulosic matrix of MSW (and DSS or sylvan waste) serves to encapsulate crushed caking coals (including fines) so the normally exuded tars are not permitted to agglomerate the charge, but are contained until they are cracked to noncondensible gases in the pyrolysis section of the gasifier. The realization of this objective requires the production of sturdy briquettes from a blended mixture of such disparate components as shredded MSW, crushed coal, dewatered sewage sludge, and binder ingredients such as "black liquor" and lime (the latter serving also as a sulfur-fixing scavenging component).

A significant accomplishment of the Phase II-C program was the development in standard commercial equipment of a briquetting process that produces Simplex briquettes which have proved noncaking in slagging gasifier operation and which possess high-structural integrity to withstand the compression and attrition they will experience in gravitating through the drying, pyrolysis, and reaction zones of the gasifier. Approximately 40,000 Simplex briquettes, comprising a number of optimized formulations, were produced in 2 days of operation at the Bepex pilot plant facility in Chicago. These briquettes will be employed as feed material in a number of semicontinuous runs to be performed in the Simplex PDU at Columbia University. The Phase II program also demonstrated that shredded wood waste or forest pulp could be substituted for MSW as the tar-containing cellulosic component in Simplex briquettes. This finding is now being implemented and developed under sponsorship of the Energy Research and Development Authority of the State of New York. Similarly, it has been demonstrated that dewatered sewage sludge can be effectively incorporated in the Simplex formulation. The MSW or refuse-derived fuel contributes to the structural strength of the briquette and the presence of coal provides abundant energy to sustain the drying and pyrolysis of the water-freighted sewage sludge solids. This modification of Simplex, termed Sanoplex, is being considered for development by the Environmental Protection Agency.

PLANS FOR THE COMING YEAR – The Phase II-D process development program currently in progress will continue to evaluate such features of the Simplex process as the superimposition of the water-gas-shift reaction in the primary gasifier through the introduction of superheated secondary steam to the high-temperature reaction zone at a temperature of about 2000°F, if it is desired to produce a hydrogen-rich synthesis gas; and the incorporation of lime or dolomite in the briquette formulation to serve as a sulfur getter when processing high-sulfur coals. Semicontinuous "steady state" runs are projected to verify noncaking behavior for a number of commercially important coal/biomass ratios.

Upon completion of Phase II, it is proposed to employ the 25-t/d slagging gasifier at the Grand Forks Energy Technology Center as a test bed for the pilot demonstration (Phase III) of the

Simplex process. Implementation of the pilot plant program calls for the production of 250 to 450 tons of Simplex briquettes in commercial rotary press equipment to serve as feed for a series of 3-day continuous runs with a number of optimized briquette formulations that have proved successful in steady-state bench-scale runs at the Columbia test facility. Given the successful completion of these pilot plant runs, demonstrations runs will be conducted on a modular scale of 500 t/d, employing an existing oxygen-refuse converter that is potentially available on lease to this project.

HYDROGEN ATTACK IN CR-MO STEELS AT ELEVATED TEMPERATURES

CORNELL UNIVERSITY
DOE - $199,971; Cornell U - $11,467
9/1/78 - 8/31/80
Principal Investigator - Che-Yu Li

OBJECTIVES — Cr-Mo steels have been identified as potential structural materials for coal-conversion plants. This project is designed to obtain microstructure and mechanical property data of these steels under the simultaneous influence of high-temperature and high-pressure hydrogen and applied stress. The work will include experimentally determining the kinetics of nucleation and growth of gas bubbles or cavities in 2-1/4 Cr-1-Mo steels at elevated temperatures under the influence of high-pressure hydrogen and applied stress; and developing kinetic equations for estimating the number, density, and size distribution of grain-boundary bubbles or cavities as a function of time under conditions of interest to coal-conversion plant operations.

For piping and pressure-vessel design for service at elevated temperatures, the design criteria are usually based on deformation limits due to creep, stress-to-rupture life, and creep-fatigue interaction effects for thin-wall components and on crack-growth rate and fracture toughness for thick-wall components. The existence of grain-boundary bubbles or cavities is expected to influence all of these mechanical properties.

RECENT WORK AND ACCOMPLISHMENTS — Present efforts in the reporting period have been concerned with obtaining suitable specimens, developing new equipment and activating existing equipment, and performing preliminary tests to determine the experimental conditions of interest. The materials selected for the present work are 2-1/4 Cr-1-Mo steels, particularly ASTM A387 and A542. A major portion of the work will investigate the A387 steel. The materials have been obtained, and some specimens have been machined.

Three main experimental conditions must be controlled for the nucleation and growth studies: temperature, applied stress, and hydrogen pressure. The necessary equipment is being put into operation. In particular, a creep stand enclosed in a high-pressure hydrogen chamber has been designed and is under construction to perform experiments at elevated temperatures, with applied stress and in a high-pressure hydrogen environment.

PLANS FOR THE COMING YEAR — The planned research can be divided into three parts: Task I, cavity nucleation studies, Task II, cavity growth studies, and Task III, data analysis. In Task I, the rate of nucleation of grain-boundary bubbles or cavities in 2-1/4 Cr-1-Mo steels will be measured as to temperature, hydrogen pressure, and applied stress. The steel specimens will be exposed to high-pressure hydrogen up to 2000 psi at elevated temperatures (350^o to 600^oC) in autoclaves with or without applied stress. Stress levels will be up to the yield strength for a given temperature. After a specified exposure, the specimens will be examined with scanning electron microscopy and other metallographic tools to determine the number, density, and size distribution of the bubbles or cavities based on which rate of nucleation can be estimated. In Task II, the rate of growth of grain-boundary bubbles or cavities in 2-1/4 Cr-1-Mo steels will also be measured as to temperature, hydrogen pressure, and applied stress. Growth experiments will be conducted at elevated temperatures (350° to 600°C) with internal methane pressure as the driving force in a high-pressure environment. Hydrogen pressures up to 2000 psi will be used. In addition, growth experiments will be performed outside the hydrogen environment under applied stress at elevated temperatures (350° to 600°C). In Task III, the experimental data will be analyzed to determine useful correlations for the number, density, and size distribution of grain-boundary bubbles or cavities in 2-1/4 Cr-1-Mo steels under the conditions investigated and for extrapolation to other conditions not investigated experimentally but pertinent to coal-conversion technology.

THERMAL EFFECTS DURING MATERIAL CONVERSION AND CATALYSIS

NEW YORK UNIVERSITY
DOE - $118,000; NYU - $3412
3/15/76 - 3/14/79
Principal Investigator - J.M.D. Low

OBJECTIVES — Because heterogeneously catalyzed processes will play a dominant role in the actual and potential processes for converting coal to gaseous and liquid fuels, it is important to have information about the nature and properties of solid catalysts and the operating parameters of the heterogeneously catalyzed reactions. One of these parameters is temperature. However, the important criterion is not necessarily the easily measured average temperature of the bulk-reacting mixture, but is the actual temperature at the region where the reaction is occurring at the surface of the solid catalyst. There is very little factual information about such surface temperatures.

Variation in temperature can affect the overall economics of a catalytic process by changing the activity and selectivity, and excessive increases in temperature can result in costly damage to the catalyst and to processing equipment. Consequently, a program of work has been started to define temperature effects so that processes may be improved. The objective of this program is to perform a series of experiments to measure temperatures, both average and transient, of the surfaces of coal-conversion catalysts, using a contactless, radiometric method. The data obtained from the experiments will be used to suggest methods of minimizing aging and/or sintering of catalysts, improvements in catalyst design and fabrication, improved catalyst regeneration procedures, and methods of optimizing reaction conditions.

RECENT WORK AND ACCOMPLISHMENTS — A multiple-reactor system suitable for observing temperature fluctuations of solid surfaces has been constructed. A reactor consists of a heated tube fitted with an infrared-transmitting window directly above the solid. Streams of reactant gas are blended and passed over the solid, and temperatures are determined by measuring the infrared radiation emitted by the solid. Data concerning the average and transient temperatures have been obtained under reaction conditions. The reactions have included the burn-off of catalytic coke from Pt-alumina and Pt/Re -sieve catalysts; the oxidation of charcoal, pyrophoric iron, and Raney Ni catalysts, and the oxidation, regeneration, and coke burn-off of Ni-silica.

A system consisting of an apparatus to activate Raney nickel (as fine particles deposited on wire), a reactor plus gas chromatographic analysis system suitable for carrying out the methanation reaction, and an infrared microscope-pyrometer has been constructed. The system will measure temperature fluctuations of the Raney nickel particles during reaction conditions.

PLANS FOR THE COMING YEAR — Measurements with the microscope-radiometer system will be made.

FLUID DYNAMICS OF A FLUIDIZED BED PACKED WITH HEAT EXCHANGERS

NEW YORK UNIVERSITY
DOE - $1,023,772; NYU - $40,576
2/1/76 - 4/30/80
Principal Investigator - V. Zakkay, G. Miller

OBJECTIVES — Several advanced approaches for using coal to produce electricity are being developed. In one of these approaches, the coal is burnt under pressure or at atmospheric conditions in a fluidized bed that contains a heat-exchanger configuration (where steam is produced) and a volume of small solid particles that distribute the heat and absorb the sulfur dioxide. Present equipment includes a facility built by Pope, Evans, and Robbins at Rivesville, West Virginia, and a pilot plant at the Exxon Research and Engineering Company. The bed at Rivesville operates at atmospheric pressure and uses a horizontal tube concept based on standard boiler designs. This research is performed in support of the Rivesville program, as well as in support of pressurized fluidized beds such as the Exxon and Curtiss Wright designs. The research provides information on efficient methods of extracting heat from fluidized beds. Both the 1- and 3-ft-diameter fluidized beds have been completed. Heat-transfer data have been obtained for several geometries of the heat exchanger (horizontal and vertical) and for various injection profiles of both velocity and temperature at the distributor plate. Design criteria have been established for both pressurized and unpressurized systems to be used for increasing circulation within the bed. This information can be used for large plants to extract large amounts of heat from a fluidized bed.

RECENT WORK AND ACCOMPLISHMENTS — A major portion of the effort involved the design, construction, and installation of the components for conversion to coal firing. Included in this effort was the completion and installation of the coal feeder and coal storage equipment, the design, construction, and installation of a cyclone system and a metered-exhaust system, the lining of the entire fluidized bed with aluminum oxide firebrick, and the completion of the entire fluidized bed assembly. An additional effort included converting the 1-ft bed to coal combustion. The following research has been accomplished in the 1-ft bed: (1) the utilization of vertical fins on vertical heat-exchanger tubes had a minimum impact on the overall heat that was extracted from fluidized bed; (2) heat-exchanger configurations in deep beds, in which the ratio of settled bed height to bed diameter is large, experienced highly non-uniform local heat-transfer coefficients as a function of bed height; and (3) initial results of a test program assessing the effect of heat exchanger solidity (ratio of heat exchanger surface area to boiler cross section area) for a vertical configuration on heat transfer in a fluidized bed indicated that the basic criterion for keeping the solidity below 10 percent in order to keep a good level of fluidization in the bed is too conservative.

PLANS FOR THE COMING YEAR – The present contract extension was initiated in September 1978. Work has been completed on the conversion to coal. Coal combustion tests will be performed, and the configurations tested last year with propane gas will be repeated. All of these tests will be conducted in the modified coal-fired 1-ft bed.

DESULFURIZATION WITH TRANSITION METAL CATALYSTS

STATE UNIVERSITY OF NEW YORK AT BINGHAMTON
DOE - $39,932
8/1/77 - Continuing
Principal Investigator - J.J. Eisch

OBJECTIVES – This study evaluates the mechanism and efficiency of novel, homogeneous transition-metal desulfurizing agents for organosulfur compounds. Because the molecular structures present in native coal contain organosulfur subunits, efficient, homogeneous desulfurizing agents may be useful in studies of coal structure itself. Moreover, these same agents, if active catalytically, would be valuable in freeing fuels or organic chemicals obtained by coal pyrolysis from the contaminating organosulfur components. To this end, the desulfurizing action of nickel, molybdenum, cobalt, iron, titanium, and tungsten, in combinations with certain nitrogen, phosporus, and olefin ligands, is being evaluated in their behavior toward diaryl sulfides, alkyl aryl sulfides, dialkyl sulfides, mercaptans, and sulfur heterocycles. By using a variation of ligands, solvents, and hydrogen sources, desulfurizations under mild conditions are being sought, first with stoichiometric reagents and then in catalytic processes.

RECENT WORK AND ACCOMPLISHMENTS – As model systems for desulfurization, aromatic organosulfur heterocycles (E = NH, O, S or σ-bond) have been studied. These systems are typical of the stable organosulfur compounds found in coal-derived fuels. Carbon-sulfur bonds of this kind may also be present in certain native coals.

In the first phase of this study, effort has been directed toward finding stoichiometric reagents capable of desulfurizing these systems under mild conditions ($<100^{o}$C and at low pressure). By using bis-1,5-cyclooctadiene-nickel (0) in the presence of α,α^1 -bipyridyl in tetrahydrofuran at 40^{o} to 60^{o}C, two types of desulfurization have been observed. Both of these desulfurizations occur below 100^{o}C and in the absence of hydrogen gas. Continuing studies of the mechanisms of these different processes have shown that organonickel intermediates are involved and that these accept hydrogen from either HCl or $LiAlH_4$.

The effects of solvent, ligand, metal, and hydrogen on the overall rate of desulfurization are being studied. A survey of the desulfurizing action of these reagents on open-chain compounds has already begun. Such sulfides as dibenzyl sulfide are smoothly converted into toluene by this reagent. However, benzyl mercaptan yields both toluene and bibenzyl.

PLANS FOR THE COMING YEAR – A survey of the desulfurizing action of these stoichiometric reagents toward other types of organosulfur compounds is underway. The catalytic activity of such nickel (0) systems under a hydrogen atmosphere and with various hydrogen sources will be investigated. Such studies will be extended to some recently discovered titanium reagents.

OPTIMIZATION OF BACTERIAL LEACHING FOR REMOVAL OF PYRITE FROM COAL

STATE UNIVERSITY OF NEW YORK AT BINGHAMTON
DOE - $19,500; SUNY - $2400
8/1/77 - 10/31/78
Principal Investigator - N. Lazaroff

OBJECTIVES — This research seeks to test and improve laboratory-scale bacterial leaching systems as models for industrial removal of pyritic sulfur from aqueous slurries of crushed coal. Increased use of coal as an energy source partly depends on development of low-cost, desulfurized, environmentally acceptable fuel from abundant high-sulfur eastern bituminous coals. The bacterial catalyzed process by which pyrite is leached from coal occurs at a significant rate, under natural conditions in coal seams exposed to air and water, leading to the serious pollution problem of acid-mine drainage. This fact can be exploited by using coal slurries to produce depyritized coal under controlled conditions so as to yield a more suitable slurry for noncorrosive transport, as well as byproducts of commercial significance that would help defray the cost of desulfurization and mine-water transport.

RECENT WORK AND ACCOMPLISHMENTS — An improved laboratory leaching system consisting of an air-lift percolator and a magnetically operated stirrer in a horizontal multiple-chambered vessel, has been further operated and tested. The air-lift circulates mine water or other lixiviants containing iron-oxidizing bacteria and suspended coal particles through the chambers. The stirrer resuspends coal particles that form heavier aggregates as leaching proceeds. The aggregation is due partly to bacterial formation jarosite, which penetrates and coats the coal particles. The net result of this operation is the transfer of leached slurry to a chamber in which resuspension does not occur and the coal particles settle out. At this point, the bacterially treated particles are treated with dilute NH_4OH, which converts adherent jarosite to $Fe(OH)_3$ and extracts SO_4^{2-} from the jarosite. The leaching system operates by continuously feeding on a slurry of coal in lixiviant and recovering depyritized coal. Between 30 and 40 percent of the total sulfur, in coals containing more than 2.5 percent sulfur, was removed within 10 days of leaching, which amounts to 60 to 70 percent of the pyritic sulfur in most cases.

Studies on six eastern coals indicated that the key to extraction of pyritic sulfur from coal by bacterial leaching is the removal of the jarosite formed in the presence of sulfate concentrations. Treatment with ammonium hydroxide is one of several methods considered for extraction of the sulfate from adherent jarosite. This method offers the following advantages: recovery of ammonium sulfate as a byproduct; formation and recovery of ammoniojarosite, for use as an iron, sulfur, nitrogen fertilizer., and recycling of NH_4^+ and SO_4^{2-} to the leaching process for propagating populations of iron bacteria.

PLANS FOR THE COMING YEAR — A continuous bacterially catalyzed process will be developed for converting pyrite in coal slurries to ammoniojarosite. Jarosite biogenesis will also be undertaken to explore the role of microorganisms in the incorporation of cations in jarosites.

NITRIC OXIDE PRODUCTION FROM CHEMICALLY BOUND NITROGEN IN COAL

STATE UNIVERSITY OF NEW YORK AT BUFFALO
DOE - \$38,900; SUNY - \$11,706
9/1/77 - 8/31/79
Principal Investigator - L.A. Kennedy

OBJECTIVES – Knowledge of the foundation and control of nitrogen oxides due to the conversion of organically bound nitrogen in coal is an important area of combustion research. The present research program is a laboratory study of this problem using a vortex-stabilized combustor to examine the factors that influence the generation of NO_x from fuel-bound nitrogen. This laboratory combustor permits control over the mixing rate of the injected coal particles and allows the particle-injection pattern and the local coal particle concentrations to be varied. This permits the examination of the large range of flow parameters that could influence the combustion process. Better understanding of the factors controlling NO_x is essential in establishing techniques to minimize the NO_x emissions in future coal-burning systems.

RECENT WORK AND ACCOMPLISHMENTS – During the past year, the laboratory combustor was designed and built. The combustor is a vortex-stabilized reactor in which the concentration of powdered coal can be varied within the combustor, allowing the examination of the influence of particle-concentration density. While awaiting fabrication of this combustor, some preliminary studies were conducted in a conventional type combustor.

The first phase of this work examined the overall factors influencing fuel NO_x by monitoring the concentration of the various combustion products at the exit plane of the combustor. The fuel NO_x was separated from that originating from atmospheric fixation by burning the coal particles in a nitrogen-free mixture of an oxidizing gas rather than air. Comparisons could then be made between NO_x formed from coal combustion in air and that of the nitrogen-free oxidizer by matching the flame temperatures obtained from burning the coal in air and the tailored oxidizing gas mixtures together with the flow patterns at various equivalence ratios. The laser-doppler anemometer system determines the inlet and exit velocity distributions for both gases. Matching the peak temperature and the inlet and exit velocities ensures that the dynamical behavior of the two systems is similar.

PLANS FOR THE COMING YEAR – Measurements of NO_x emission will be examined for different coals and for various fluid mechanical conditions within the combustor. The influence of temperature upon NO_x generated by organic fuel compounds will be studied. Coal chars will also be used in a set of experiments.

NOVEL CATALYST SUPPORTS FOR HYDRODESULFURIZATION OF COAL

STATE UNIVERSITY OF NEW YORK AT BUFFALO
DOE - \$243,553; SUNY - \$56,187
6/3/75 - 5/31/79
Principal Investigator - S. Weller

OBJECTIVES – The objectives are to prepare and evaluate novel desulfurization catalysts of varying but controlled pore size, in both particulate and monolith configuration, to develop physicochemical methods for measuring the specific surface area of supported MoO_2 or MoS_2 in desulfurization catalysts, new or used, and to study catalytic activity in model test reactions.

RECENT WORK AND ACCOMPLISHMENTS – Four Al_2O_3 supports with average pore diameters of about 100, 200, 500, and 1000Å were used; each showed unimodal and sharp distribution of pore size. Autoclave tests of unsulfided catalysts made from each Al_2O_3 indicated that the optimum pore diameter was about 200Å. Even with an excess of a hydrogen-donor solvent (tetralin), the use of N_2 instead of H_2 results in lower liquefaction and lower desulfurization. Presence of Mo/Al_2O_3 catalyst has a major effect on the conversion of asphaltene to oil as well as on hydrodesulfurization; therefore, liquefaction, even in excess of a hydrogen-donor solvent, benefits from the presence of H_2 and catalyst. Monolith $Co/Mo/Al_2O_3$ catalysts of three different configurations have been prepared from pure Al_2O_3 monoliths. Highest oil yields from coal are achieved with monolith catalysts that have 200 square channels/in.^{2}, presumably because of easier flow through the larger channels. Techniques have been developed for preparing pelleted MoO_3-Al_2O_3 catalysts in which MoO_3 is present as a thin shell near the outer surface of the pellets and for using O_2 chemisorption at low temperature to measure the specific surface area of molybdena in a reduced MoO_3-Al_2O_3 or CoO-MoO_3-Al_2O_3 catalyst. The data imply that in reduced catalysts the MoO_2 exists as small crystallites covering about 25 percent of the total surface. Two model reactions have been found useful. Hydrotreating of thiophene in a pulsed microreactor can discriminate between catalytic activity for hydrodesulfurization, olefin hydrogenation (of the butene products), and olefin isomerization. Hydrotreating of methyl naphthalene in an autoclave can discriminate between ring hydrogenation, hydrodemethylation, and ring hydrocracking to give substituted benezenes.

SURFACE PHENOMENA IN DEWATERING COAL

SYRACUSE UNIVERSITY
DOE - \$75,799
6/75 - 6/78
Principal Investigator - D.V. Keller

OBJECTIVES – As hydrobeneficiation techniques strive to reduce pyritic sulfur and other mineral matter in coal, the need for handling fine coal becomes essential. The product coal from these processes contains between 5 to 15 percent water depending on coal maceral distribution, size, mineral matter, and water purity. Any decrease in the water concentration of the product coal is a significant economical and technological advantage to the industry. The purpose of this research program is to expand, on a scientific basis, this knowledge which is already available to the industry. A minor objective of the investigation is the examination of the effect of the presence of electric fields on dewatering.

RECENT WORK AND ACCOMPLISHMENTS – The influence of certain surfactants on the dewatering of fine coal has been investigated. These surfactants were found to effect the pressure differentials required for dewatering as well as the residual water contents of the coal beds attainable by this dewatering. Both effects were attributed to surfactant adsorption.

Adsorption at the liquid-air interface resulted in a decrease in the interfacial tension between the two phases. The effect of this decrease on the pressure differentials required for dewatering agreed with that predicted by the capillary theory applied to the system. Adsorption at the solid-liquid interface was correlated with the complex behavior of the residual water contents as a function of surfactant addition. A comprehensive model, designed for the adsorption of the surfactants onto the coal, allowed the mode of physiosorption to change as the amount of surfactant adsorbed increased. By using the model, consistent and reasonable results were found for the specific surface area of the coal and for the standard free energies of adsorption. The model was also found to be appropriate when considering the heterogeneous nature of the coal. Furthermore, the hydrophobicity of the molecular groups of the molecules, expected from the model to be controlling the hydrophobicity of the interface, agreed with that predicted by other means.

PLANS FOR THE COMING YEAR – A final report was submitted to DOE. No extension of this program is anticipated.

ENHANCED COMBUSTION OF FOSSIL FUEL PARTICLES AND DROPLETS IN OSCILLATING FLOW

SYRACUSE UNIVERSITY
DOE - $50,000; Syracuse U - $4700
9/1/78 - 8/31/80
Principal Investigator - F.A. Lyman

OBJECTIVES – This program will determine the effect of oscillating flow on the rates of combustion of fossil fuel particles and droplets. Under certain conditions, oscillating combustion may result in significantly increased rates of burning and thus provide more effective fuel utilization, with reduced excess air and improved combustion efficiency. Better understanding of the combustion process in oscillating flows is needed to establish the conditions under which significant improvements in burning rate will be attained. Captive-particle experiments will be performed to determine the dependence of burning rate on particle size and composition and oscillation amplitude and frequency. A theory will be developed to facilitate interpretation of the results.

RECENT WORK AND ACCOMPLISHMENTS – An apparatus to produce an oscillatory air flow of high amplitude and controlled frequency has been designed and built. The apparatus consists of a resonance chamber acoustically coupled with a tubular test section in which captive particles of char or coal will be burned. Tests to determine the amplitude and frequency of the oscillating velocity in the test section are underway. Holders for small fuel particles have been constructed by drawing down thin quartz solid or tubular filaments. The particles will be held at the end of the solid or tubular filament by cement or vacuum, respectively. The particles are to be ignited by radiation; but after some difficulties were encountered by igniting them with focused light from a filament-type projection lamp, an electrically heated nichrome wire coil surrounding the particle was used. A review of the literature on pulsating combustion has been completed, and progress has been made on formulating a theoretical model to predict the dependence of burning rate on the amplitude and frequency of the oscillating flow.

PLANS FOR THE COMING YEAR – Calibration of the oscillating flow chamber will be completed. Burning rates of nonvolatile carbon or char particles will be measured in the test section with and without oscillating flow, using high-speed cinematography and/or a light emission-monitoring system consisting of a fiber optics probe and photomultiplier. Formulation of the theoretical model will be completed and numerical computations performed to predict the burning rates of nonvolatile solid fuel particles, to compare with the experimental results and indicate other regimes of parameters to be investigated experimentally. Consideration will be given to the effect of gas-pause combustion of volatile particles and droplets in oscillating flow.

CATALYTIC COAL GASIFICATION WITH MOLTEN SALTS

UNIVERSITY OF ROCHESTER
DOE - $99,556
9/1/78 - 8/31/80
Principal Investigator - H. Saltsburg

OBJECTIVES — Since alkali carbonates are known catalytic agents for coal gasification, the objective here is to examine the role of $[CO_3^=]$ in this process by monitoring the related oxygen activity $[O^=]$ in a catalytic molten salt in addition to the usual gas phase parameters P_{CO_2}, P_{H_2O}. The use of pure molten carbonates presents technical problems in using high-temperature, corrosive, and hydrolytically unstable materials. An understanding of the catalytic chemistry may make it possible to utilize lower melting, less corrosive melts as catalysts or as catalyst solvents (favoring direct methanation), and the alteration of product selectivity by chemical means in the solvent melt will be explored.

RECENT WORK AND ACCOMPLISHMENTS — All work has involved the acquisition and set up of the appropriate laboratory equipment. A reaction cell in which the molten salt can be studied has been built; the flow system for the reactor has been assembled.

PLANS FOR THE COMING YEAR — Since the properties of the pure molten salts will be of interest as a fiducial point, the measurement of oxygen activity in alkali carbonates (pure and eutectic mixtures) and hydroxides will be made. Both temperature P_{H_2O} and P_{CO_2} over the melt will be controlled. Carbonates dissolved in other solvent melts will be studied also. The gasification rate and product distribution with both CO_2 and H_2O as active agents will then be examined for these melts. Both precharred and unprocessed coal powders will be investigated. From these melts, an assessment of the role of $[CO_3^=]$ will be made.

APPLICATION OF SOLID ELECTROLYTE MATERIALS FOR CARBON-ION TRANSPORT IN FUEL CELLS

DUKE UNIVERSITY
DOE - $24,600
9/1/78 - 8/31/79
Principal Investigator - F.H. Cocks

OBJECTIVES — This project has set out to demonstrate and measure the ionic conductivity, mobility, and transference numbers for carbon-doped refractory metal oxides and other high-temperature, carbon-bearing materials. These measurements will be carried out using the three-point, direct-current polarization technique, as well as the classical reversible electrode method. To determine in advance the ability of a given material to transport carbon-ions, the crystal structure and the concomitant influence of carbon on this structure should be studied. This is being done by direct X-ray methods.

RECENT WORK AND ACCOMPLISHMENTS — Work to date includes the examination of candidate refractory oxides and other carbon-bearing materials both crystallographically and electrically. Experimentation with prototype measurement support systems, a reversible electrode system, and electronic measuring circuits has been conducted. The crystallographic experiments have entailed primarily defractometry, Laue, and Debye-Scherrer techniques. In addition, pressing and sintering techniques for preparing fully dense samples have been perfected.

PLANS FOR THE COMING YEAR – The survey of candidate electrolytes and reversible electrode materials will be continued. With measurement techniques available for transference numbers and ionic conductivity, the procedure will examine systematically promising materials both as functions of stoichiometry as well as functions of preparation techniques. The properties of crystal structures likely to show carbon ion mobility can be enhanced by dopants. Therefore, candidate materials and the effects of dopants on both crystal structure and ionic conductivity will be studied.

DETONATIVE COAL GASIFICATION

NORTH CAROLINA STATE UNIVERSITY
DOE - $19,800; North Carolina SU - $10,000
9/1/77 - 8/31/78
Principal Investigators - T.H. Pierce, E.M. Afify

OBJECTIVES – The main objective of this research is to theoretically and experimentally study the extent to which a hydrogen-oxygen detonation wave is capable of effecting gasification of pulverized coal.

RECENT WORK AND ACCOMPLISHMENTS – A one-dimensional analysis of the response of a single coal particle within the expansion-wave region behind the detonation front is presented. Independent variables in addition to coal type include particle diameter, initial H_2-0_2 ratio, and expansion-wave length (at the time the particle is overtaken by the detonation front). The most significant result of this analysis is the prediction of relative gas/particle velocities ranging from 125 to 1500 m/sec, which are sustained throughout particle residence times of 1 to 15 m/sec corresponding to 10 to 1000 micron-diameter particles.

An experimental facility comprising a 47-m-single shot detonation duct was constructed for this study. The duct is a 2.54-cm square section and is terminated at both ends by 0.36-m-diameter x 2.44-m-long cylindrical tanks which contain helium gas during testing. Sized coal particles are placed in the first 3.7-m length of the duct, and thin brass diaphragms initially separate the duct from the two helium tanks. A piping system was designed and constructed to fill the detonation duct with a mixture of hydrogen and oxygen at different ratios. Detonation is initiated at the duct end closest to the coal particles by a capacity discharge ignition circuit. The diaphragm at that end bursts allowing combustion and gasification products to exhaust into the adjoining tank where they are quenched and decelerated. When the detonation reaches the far end of the duct, the second diaphragm bursts, minimizing wave reflections that would otherwise return to the "test section" end and interfere with the flow field. After testing, the contents of both tanks and the duct are circulated and mixed. A gas sample is then drawn and analyzed for yield. Although few tests were conducted for reporting conclusive observations, in two experiments yields of CO and CH_4, representing about 40 percent of the total initial carbon content in the samples, were obtained.

PLANS FOR THE COMING YEAR – This project has been terminated.

CHEMISTRY OF LIGNITE LIQUEFACTION

UNIVERSITY OF NORTH DAKOTA
DOE - $551,400; North Dakota U - $135,657
1/1/76 - 6/30/79
Principal Investigator - V. Stenberg

OBJECTIVES – This project seeks to compare samples of solvent-refined coal (SRC) and solvent-refined lignite (SRL) to aid in the development of analytical methods for SRC, SRL, and their heavy liquids, and to investigate the mechanism of solvent refining using carbon monoxide-water and carbon monoxide-hydrogen water blends of reducing gases. Catalysts for upgrading SRC and for carbon monoxide reductions are being studied.

RECENT WORK AND ACCOMPLISHMENTS – SRL, obtained by treating lignite with carbon monoxide-hydrogen-water at 1500 to 2500 psi at about 400°C, has the molecular weight range of 4000 to 160 g/mol, with 460 as the average, depending on the conversion conditions. One-half of the oxygens of SRL are ethers and one-half are phenolic. SRL is similar to SRC from bituminous and subbituminous coals in C, H, and S elemental analysis, acid content, NMR, ESR, and UV spectra, but lower in nitrogen and base content. A method has been developed for determining the percent of acidic hydrogens present in SRL and SRC samples based acetylation. Hydrogen bonding, due to phenols and possibly carbazoles, is one of the major forces determining benzene solubility of SRL. The soluble portions of SRL from various solvents was found by NMR to reflect the aromaticity for the whole sample to a very high degree. However, the benzene insoluble portions contain more poly-condensed aromatic compounds. S-Triazene was found to be a superior solvent for carbon 13 NMR. The presence of tetralin has little or negative effects on eight model compound conversions. Sodium carbonate and ferrous sulfide gave mixed results for conversion of the eight model compounds; however, both favored denitrification of quinoline. A blend of carbon monoxide-water and hydrogen was the optimum set of reducing gases for all model compounds but quinoline. Two samples of fly ashes out of six tested were better catalysts for conversion than sodium carbonate using carbon monoxide and water. Evidence has been discovered for a new reduction mechanism for organic molecules by carbon monoxide in which there is a transfer of electrons from the catalyst surface to carbon monoxide. Of a host of metal oxides tested, only the alkaline earth oxides have indicated surface-bound CO.

PLANS FOR THE COMING YEAR – Under a new proposed contract, studies will continue with research on the structure of coal liquids produced under different conditions; the structure of lignite and other coals; mechanistic and catalytic studies of H_2, CO, and/or water reacting with model compounds and polymers; and electron spin resonance studies of CO and/or organics on catalysts.

CHEMICAL MODIFICATION AND SEPARATION OF PREASPHALTENES OF SRC

UNIVERSITY OF NORTH DAKOTA
DOE - $99,300
9/15/78 - 9/14/80
Principal Investigator - N.F. Woolsey

OBJECTIVES – The preasphaltene content of coal-derived fuels results from incomplete hydrocracking of the coal molecules. In order to understand and modify the hydrocracking procedure to give better fuels, a study of the chemical structure of preasphaltenes is necessary. The intractable nature of preasphaltenes (soluble only in pyridine) impedes application of many structural techniques. The object of this study is to solubilize preasphaltenes by rational chemical modification and to apply gel-permeation chromatography as an initial step in their structural determination. Two chemical procedures will initially be investigated: solubilization by acetate formation or by ether cleavage or a combination of both techniques.

RECENT WORK AND ACCOMPLISHMENTS – The project has been partially staffed and preliminary work begun. Using a radiochemical labeling technique, the C acetylation as well as 0 acetylation has been demonstrated under standard literature conditions.

PLANS FOR THE COMING YEAR – Staffing will be completed, and the development of the acetylation procedure will continue until conditions for only 0 and N acetylation have been found. This technology will then be applied to preasphaltenes of solvent-refined coal (SRC), followed by solubility determinations and subsequent gel-permeation chromatography. Initiation of ether cleavage studies is anticipated about mid-year with attempts to cleave some untested model compound, particularly diarylethers. Once the range of reactivity has been established for the ether cleavage methods, application to preasphaltenes will begin.

OXYGEN STOICHIOMETRY AND ANALYSIS OF COAL, LIGNITE, COKE, AND DERIVATIVES

NORTH DAKOTA STATE UNIVERSITY
DOE - $49,135; NDSU - $18,000
2/28/76 - 6/30/78
Principal Investigator - A. Volborth

OBJECTIVES – This project involves an investigation of how an accurate oxygen determination can affect material balances obtained in the analysis of coal, ash, and derived carbonaceous products, as well as how it affects the interpretation of the analytical results. In this work, oxygen is determined accurately, rapidly, and relatively inexpensively by fast-neutron activation (FNA) analysis, replacing the conventional "oxygen by difference" method. The data obtained are then used in improving the correlation of chemical and physical properties, such as reactivity and viscosity, with oxygen content.

RECENT WORK AND ACCOMPLISHMENTS – FNA oxygen analyses, which require only 30 sec, have been found sufficient to rank coal. Such data make possible improved interpretation by engineers of oxidation and reduction processes such as liquefaction, gasification, and solvent refining. Thus, monitoring changes in oxygen content can provide valuable information regarding the effectiveness of an industrial process and its component steps. Preparation of correlation charts is underway.

PLANS FOR THE COMING YEAR – The contract has been completed.

COAL AND CHAR REACTIVITIES

CASE WESTERN RESERVE UNIVERSITY
DOE - $320,923; CWRU - $14,555
6/1/76 - 11/30/78
Principal Investigators - J.C. Angus, N.C. Gardner

OBJECTIVES – The principal objective is to measure coal and char reactivities in environments representative of commercial processes for coal gasification. The results will be used to provide data for assigning large-scale gasification plants. Secondary objectives include determining rate expressions and mechanistic interpretations for the coal gasification process at practical conditions and determining whether catalytic gasification can increase reactivity and provide increased primary methane yields.

Because of the capital-intensive nature of coal gasification plants, there is a great economic incentive for systematic design and optimization of these commercial processes. There is, however, very little accurate gasification rate and gas composition data taken at practical process conditions to use in reactor models. Therefore, independent *a priori* calculations of maximum plant throughputs cannot be confidently made. The present project is directed toward providing the required data.

RECENT WORK AND ACCOMPLISHMENTS – The second-generation thermobalance reactor was designed and constructed. The thermobalance employs a novel means for obtaining the kinetic data, in that the entire reactor plus contents will be weighed during the course of a run, rather than simply weighing a hanging basket within the reactor core. This procedure permits duplication of conditions existing within a commercial reactor much more closely than can be achieved with a conventional thermobalance. In particular, the product gas stream composition, the flow regime within the reactor, and the initial heatup period can be more representative of commercial large-scale reactors. The new reactor provides a unique method for measuring coal and char reactivities at practical operating conditions. The second-generation thermobalance is being used to make differential rate measurements for a series of chars at representative commercial-operating conditions. These data are used for construction of kinetic-rate expressions using techniques developed in the laboratory. Particular attention is paid to the influence of extent of carbon conversion and catalysts on activation energies, surface areas, and pore structure.

The steam gasification of Synthane chars was performed in an existing integral reactor. Uncatalyzed chars and chars with alkali metal and alkaline earth catalysis were studied. In addition, extensive measurements of composition changes in the product gas sampling lines were performed. Also, single-particle mathematical modeling of the gasification process has been performed. The effects of carbon conversion on porosity, specific surface area, and the reaction rate constant have been included.

PLANS FOR THE COMING YEAR – The present contract will be extended 6 months.

ELECTROCHEMICAL DISPOSAL OF H_2S

CASE WESTERN RESERVE UNIVERSITY
DOD - \$38,893; CWRU - \$3637
8/31/77 - 8/30/79
Principal Investigators - C.B. Brosilow, J.C. Angus, U. Landau

OBJECTIVES – The purpose of this research is to obtain experimental data on the direct electrolysis of liquid H_2S to elemental S and H_2. The information on anodic and cathodic products, overvoltages, and current densities will be used to make a preliminary estimate of whether an electrochemical process for H_2S disposal, which will also deliver net electrical work, is technically and economically viable.

RECENT WORK AND ACCOMPLISHMENTS – Electrolysis of liquid H_2S at both cryogenic and room temperatures has been accomplished. Pyridine was used as an electrolyte. Gaseous hydrogen was evolved at the cathode, and elemental crystalline α-sulfur was the anodic product. At very low densities, the sulfur dissolves in the liquid H_2S which prevents the formation of an insulating layer of sulfur on the anode. Preliminary measurements indicated cathodic current efficiencies were as high as 99.5 percent, and anodic efficiencies were 86.3 ± 3.6 percent. The cause of the low anodic efficiencies has not yet been identified. Parallel reactions or systematic errors in the analytical procedures are possible. The major source of voltage loss is solution resistance.

PLANS FOR THE COMING YEAR – The principal goals in the coming year are to obtain a better measure of the current efficiencies and to investigate a selection of alternate electrolytes that might reduce the solution resistivities. Of particular interest are electrolytes that will be acidic (proton donors) to H_2S and the alkaline metal sulfides. Chemically stable electrodes that can be used at high-current densities will be identified.

RECOVERY OF ULTRAFINE COAL PARTICLES BY MICROFLOTATION

OHIO STATE UNIVERSITY
DOE - \$20,000; Ohio State U - \$8571
8/1/77 - 12/31/78
Principal Investigator - A.J. Rubin

OBJECTIVES – This project will study the recovery of colloidal coal from black wash waters using novel flotation techniques. The specific objectives of this research are to develop a procedure for the preparation of colloidally stable and reproducible suspensions of ultrafine coal particles, characterize the colloid-chemical properties of these coal suspensions, investigate the feasibility of dispersed air colloid flotation as an effective recovery method under laboratory conditions, and survey the major parameters that might control the flotation process. These objectives have been met. Long-range objectives are to examine the coagulation of the colloidal coal with aluminum salts, investigate the feasibility of the microflotation technique as a recovery method, and adapt dissolved air flotation to colloid flotation and microflotation. Research has been started toward these additional objectives.

RECENT WORK AND ACCOMPLISHMENTS – Based on the results of the completed research, the following findings and conclusions are indicated: (1) stable and reproducible suspensions of colloidal coal can be produced through a process in which the coal is ground, ball milled, sieved to

-400 mesh, oxidized with hydrogen peroxide at elevated temperatures, washed and filtered, and finally resuspended in distilled water. The specific surface area of the oxidized coal particles is between 7 and 8 m^2/g; (2) the produced colloidal coal has properties similar to other negatively charged sols. Coagulation of the coal with electrolytes follows the Schulze-Hardy rule in that the plot of the logarithm of the critical coagulation concentration against counterion change is linear. The slope of this line is similar to that found with other sols. It is concluded that colloidal coal is a hydrophobic sol. The isoelectric point for the oxidized coal is near pH 1.0 as opposed to pH 5.2 for the unoxidized coal particles. Suspensions of the colloidal coal were stable above pH 3.0 whereas the unoxidized coal was unstable at pH values below 7.5; and (3) the colloid flotation of the oxidized coal can be successfully achieved using CTAB, a cationic collector, in the presence of ethanol, which was the frother used in this study. The most rapid removals were obtained in acid solutions, the optimum pH depending on the collector concentration. This pH was correlated with the isoelectric point for the oxidized coal-CTAB system. Flotation was not feasible with sodium laurylsulfate, a strongly ionized anionic surfactant collector.

PLANS FOR THE COMING YEAR — The project is complete. The results of this study are currently being prepared in a final report.

COAL HYDROGENATION VIA BONDING OF METALLIC COMPOUNDS TO COAL

UNIVERSITY OF CINCINNATI
DOE - $161,159; Cincinnati U - $10,580
4/1/76 - 3/31/79
Principal Investigator - M. Orchin

OBJECTIVES — The principal objective of this work is to determine whether covalent bonding of a metal, such as tin, directly to the aromatic structures in coal will prove to be a better catalytic system for the hydrosolubilization of coal than the same quantities of Sn added in bulk to coal. If this proves to be the case, it will be a further objective to ascertain the reasons for the superiority. An additional objective is to identify the principal chemical linkages in the coal structure which must undergo cleavage to solubilize coal.

RECENT WORK AND ACCOMPLISHMENTS — The work to date shows that the chemical incorporation of tin into a coal structure followed by hydrogenation at 375°C of such coal containing chemically bonded catalyst results in greater liquefaction than is obtained when the same level of tin is simply added to the coal. Making tin balance on the products after hydroliquefaction of coal is difficult because part of the tin appears as metallic tin, part of it remains in bound form in the insoluble fractions, and part appears in the benzene-soluble products. Mossbauer spectroscopy of tin-containing fractions shows that some tin remains in the form in which it was originally incorporated in the coal, some Sn^{2+} species are also present, and some Sn forms cannot be positively identified.

PLANS FOR THE COMING YEAR — A request for a no-cost time extension is pending approval. A critical review of the literature on the chemical solubilization of coal and on the mechanism of hydroliquefaction using both good and poor donor solvents suggests the importance of benzyl-type linkages in the solubilization processes. Experimental evidence for this theory will be obtained with particular emphasis on hydroliquefaction and reductions with metal systems.

EROSION STUDY IN TURBOMACHINERY AFFECTED BY COAL AND ASH PARTICLES

UNIVERSITY OF CINCINNATI
DOE - $164,218; Cincinnati U - $8825
8/1/76 - 7/31/79
Principal Investigators - W. Tabakoff, A. Hamed

OBJECTIVES – This program seeks to carry out experimental and theoretical studies of the erosion caused by coal and ash particles to potential turbine materials, to find the important parameters needed for basic understanding of the erosion phenomena, to study the aerodynamic effects on erosion of alloys for future turbines using coal fuel, to develop a model for predicting particle trajectories, and to develop a computer program to facilitate the prediction of erosion in turbomachinery design.

RECENT WORK AND ACCOMPLISHMENTS – During the past year, intensive testing was conducted in the stationary test erosion wind tunnel. Erosion parameters such as fluid velocity, particle velocity, particle flow rate, and particle size are controlled in this facility. The effects of variation in the specimen size, as well as the angle of incidence between the abrasive particles and the surface of the specimen, were investigated. In addition to obtaining erosion data in an aerodynamic environment, this test facility was used to determine the particle impact and rebound characteristics. The target materials used were three alloys (2024 AL, 6A1-4V Ti, and 304 stainless steel), and the abrasive particles used consisted of West Virginia coal ash. A semi-empirical equation, which was developed to predict the erosion of the test-ductile alloys, is based on the observation that the erosion process is characterized by two mechanisms, at low and high impingement angles. The empirical equation was derived to correlate the erosion damage at low, intermediate, and high impingement angles. The basic information obtained in the erosion tunnel, together with an analysis, can be used to predict the erosion of the different turbine components by ash particles. Additional testing was conducted with the new high-temperature wind tunnel, and some of the test results are already reported in the literature. This facility has the capability of providing temperatures between ambient and 2300°F for erosion testing of various materials. The effects of high temperatures on the erosion rate was determined for the three alloys. It was found that with increased temperature, the erosion rate of 304 stainless steel increases initially at a lower rate, up to a temperature of 600°R, and then increases at a much higher rate above this temperature. The design and installation of a new two-color laser anemometer system was completed and is now in operation.

PLANS FOR THE COMING YEAR – Experimental work in both wind tunnels will continue to find the important parameters that influence erosion caused by coal particles and ash. Investigation of other alloys which will be used in future gas turbines will be tested. As the experimental work is completed, the data obtained will be used in developing empirical equations for predicting the erosion rate of ductile alloys at different temperatures. The particle trajectories will be calculated using the presently obtained rebound characteristic coefficients.

REMOVAL OF ORGANIC SULFUR FROM COAL

UNIVERSITY OF TOLEDO
DOE - $50,000; Toledo U - $12,434
9/1/78 - 8/31/80
Principal Investigator - D.F. Burow

OBJECTIVES – This program is designed to carry out the initial laboratory-scale development of an efficient specific solvent extraction process for precombustion removal of organic sulfur from coal. Liquid SO_2 was chosen as the extraction medium for the following reasons: (1) available evidence indicates that a significant portion of the organic sulfur in coal is likely to be removed by extraction with liquid SO_2 at elevated temperatures and pressures; (2) the extraction medium is inexpensive and derived from the coal itself; (3) solvent and coal recovery may be accomplished using existing technology without resorting to exotic materials and methods; (4) the extracted coal will be a fine powder that is ideal for subsequent processing such as removal of inorganic sulfur, slurrying, pelletizing, or using in fluidized-bed combustion; and (5) significant cost recovery is possible because valuable feedstocks are likely to be available from the extract. Thus, the proposed process offers a unique means of reducing coal-usage costs. Because the sulfur content of many high-sulfur coals is frequently half organic, utilization of these coals often requires expensive post-combustion scrubbing or specialized fluidized-bed combustion to meet environmental standards for SO_2 emission. Thus, effective precombustion removal of sulfur from coal would substantially reduce fuel costs. The proposed process could be efficient, economical, and environmentally acceptable because the only material required would be derived from the coal itself, that is a major pollutant (SO_2) would be used to remove the source of that pollutant.

RECENT WORK AND ACCOMPLISHMENTS – Because the grant has been in effect only a short time, all work performed has been of a preliminary nature. An automated sulfur analyzer has been acquired and appropriate coal samples have been obtained.

PLANS FOR THE COMING YEAR – Work designed to establish the basic chemistry of this process and to define the optimum conditions and controllable parameters will be carried out. A variety of high-sulfur coal types will be subjected to liquid SO_2 treatment at elevated temperatures. Sulfur content of the extract and coal residue will be determined as a function of processing variables, such as temperature, coal/SO_2 ratio, coal type and form, moisture content, exposure time, and presence of reagents or catalysts. Initially, beneficiated coal samples will be examined to avoid complications in interpretation of analytical data owing to the presence of pyrite-type sulfur. Evidence that pyrite sulfur may be removable when suitable reagents are added will be investigated. Statistical methods will be used to select conditions for optimum extraction efficiency. The extract fraction will be characterized to determine its suitability as an alternative source of chemical feedstocks.

MONITORING OF MINING EQUIPMENT HYDRAULICS WITH STATISTICAL ANALOG MONITOR

OKLAHOMA STATE UNIVERSITY
DOE - $106,010
3/21/77 - 3/21/79

OBJECTIVES – This work involves the collection of data during laboratory and underground tests of coal mining equipment to establish duty cycles.

RECENT WORK AND ACCOMPLISHMENTS – Work thus far has concentrated on installing statistical analog monitors (STAMs) on new generation prototype machines being developed by DOE. More than 300 hr of data have been collected on four different pieces of equipment. The results are being used to determine that laboratory duty cycles are realistic and that components on prototype equipment are being used within their design capabilities. In addition, an improved version of the STAM has been developed that will permit rapid on-site data analysis.

PLANS FOR THE COMING YEAR – The new STAM will require Mine Safety and Health Administration (MSHA) approval for use in coal mines. More data will be collected and analyzed for prototype machines. Data will be collected from production machines to assess the potential for improvement.

CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

OKLAHOMA STATE UNIVERSITY
DOE - $318,842; Oklahoma State U- $22,893
6/9/75 - 3/8/78
Principal Investigator - B.L. Crynes

OBJECTIVES – This program will investigate catalysts for upgrading liquids from coal-to-oil processes to remove sulfur, nitrogen, and possibly other heteroatoms. Catalysts with supports of various pore sizes and pore-size distributions will be tested to seek optimum pore properties for such upgrading processes. Based on these studies, catalysts will be recommended for upgrading coal-derived liquids under hydrogen pressure to remove certain heteroatoms.

RECENT WORK AND ACCOMPLISHMENTS – Several catalysts and coal liquids have been assessed in the Catalyst Life Test Unit (CLTU), which consists of a bank of three automated trickle-bed reactors. Such activity tests are conducted from 100 to 700 hr of continuous liquid/catalyst contact. All catalysts tested revealed a significant desulfurization and denitrogenation activity loss within the first 40 to 60 reactor turnovers (time on stream divided by space time), which usually corresponds to the first 50 to 100 hr of operation. The decay rate beyond this time is lower. The liquids assessed included an FMC-COED oil, two Synthoil liquids, raw anthracene oil, and a special study liquid, Rasyn oil. Part of this study has been conducted with two vendor catalysts, Co-Mo and Ni-Mo on alumina types. A quantitative model has been developed to account for the activity decay of the catalysts. This model predicts the decay rate for those systems tested and is based upon the changes in the catalyst-support structure. Changes of the average pore size with time and the average molecular size of the coal liquid reactants are important parameters. The fractional loss in an active area is approximated by the extent of coking since carbon deposition is the primary mode of decay.

PLANS FOR THE COMING YEAR – The CLTU will be improved and portions of the project will continue on Oklahoma State University funds. The project will investigate the mechanisms of catalyst activity decay while processing coal liquids. Catalyst-aging tests will be conducted for periods of up to 30 days of continuous oil/catalyst contacting.

INTERACTION OF H-ATOMS WITH ULTRAFINE COAL DUST

OKLAHOMA STATE UNIVERSITY
DOE - $122,390; Oklahoma State U - $9338
1/1/76 - 8/3/80
Principal Investigator - G.J. Mains

OBJECTIVES – This project seeks to identify and quantify the gasoline-type hydrocarbons produced by the interaction of H-atoms with very fine coal dust above 175°C. The quantitative effects of temperature, H-atom concentration, extent of conversion, coal particle size, and concentration on product yields are primary objectives. Deductions regarding the surface and bulk molecular structures of various coals are the secondary objectives. Both the primary and secondary objectives have obvious relevance to the judicious selection of feedstock coal for liquefaction and gasification plants.

RECENT WORK AND ACCOMPLISHMENTS – The gasoline-type hydrocarbon products obtained from +35/-54 μm Illinois No. 6 coal dust have been confirmed by GC-MS. Yields and rates of production of the gaseous products have been obtained for up to 20 hr irradiation time for this size Illinois No. 6 coal. These data yield considerable insight into the surface and bulk structure of this coal. The efficiency per hydrogen atom per gram of coal was also measured as a function of time. More sensitive gas chromatography detection (flame ionization) measured gasoline-type products from the interaction of H-atoms at 200°C with subbituminous Wyoming Wyodak coal, Montana Rosebud subbituminous coal, Synthane char from Montana Rosebud, and Reading anthracite. Unfortunately, this project will terminate before these materials can be quantitatively compared with the Illinois No. 6 coal results.

PLANS FOR THE COMING YEAR – The effect of the variables, temperature, H-atom concentration, and particle size for Illinois NO. 6 coal will be determined and reported. Preliminary data on the yields of liquid products obtained simultaneously will also be quantified. The T.O.F. mass spectrometer has been retrofitted with solid state electronics to measure the products from the interaction of D atoms with Illinois No. 6 coal. The preliminary data will be correlated as well as data obtained from flash-heated solvent extraction of Illinois No. 6 coal into a coherent picture of the molecular structures of this coal and its surface.

THERMODYNAMIC PROPERTIES OF COAL-DERIVED FLUIDS

OKLAHOMA STATE UNIVERSITY
DOE - $199,640; Oklahoma State U - $10,500
3/15/76 - 3/14/79
Principal Investigator - R.L. Robinson, Jr.

OBJECTIVES – The basic goal of this project is to obtain data for components and conditions where information is lacking. The mixtures studied will approximate those which occur in the processing of coal-derived fluids. Research is divided into three major areas: (1) design, construction, and operation of a Burnett-type apparatus to measure volumetric properties (pressure-volume-temperature-composition relationship) of gases. The properties of the pure substances and selected mixtures of H_2, CO, CO_2, CH_4, and H_2O at conditions from ambient to 800°F and 2000 psia (or to the maximum temperature at which chemical reactions are unimportant) will be measured; (2) design, construction, and operation of a variable-volume, windowed phase-equilibrium cell capable of operation up to 800°F and 2000 psia. Vapor-liquid equilibrium in mixtures composed of selected light hydrocarbons/heavy aromatic hydrocarbons/water will be measured; and (3) testing and/or development of prediction methods for estimating volumetric properties and phase equilibrium in mixtures of the type studied experimentally. Results in formats suitable for use in process design calculations will be presented.

RECENT WORK AND ACCOMPLISHMENTS – Both the Burnett apparatus and the windowed phase-equilibrium cell have been designed, constructed, and tested. Data acquisition is in progress on both apparatus. To date, volumetric property measurements in the Burnett cell have been conducted on pure He, H_2C0, Ch_4, and $C0_2$ at 100°C and CH_4 at 250°C. Also, measurements have been made on mixtures of $H_2 + CH_4$, $H_2 + C0_2$, and $CH_4 + C0_2$ at 100°C, all at pressures up to 140 atm. Precision of the compressibility factors is better than 0.1 percent.

The vapor-liquid phase-equilibrium behavior of the five-component mixture of methane, ethane, propane, toluene, and 1-methlynaphthalene is currently under study in the windowed cell. Measurements are complete at 220° and 280°F at pressures up to 2000 psia. The precision of the resultant K-values ranges from 2 percent for methane to 13 percent for 1-methylnaphthalene.

PLANS FOR THE COMING YEAR – This project will terminate in March 1979. Measurements on the aforementioned systems will be continued at higher temperatures during the remainder of the project.

CHARACTERIZATION OF COAL-DERIVED LIQUIDS AND OTHER FOSSIL FUEL MATERIALS EMPLOYING MASS SPECTROMETRY

OKALHOMA STATE UNIVERSITY
DOE - $289,206; Oklahoma State U - $107,674
9/30/76 - 9/29/79
Principal Investigator - S.E. Scheppele

OBJECTIVES – This project intends to develop new and/or to refine mass spectrometric techniques for obtaining both routine and detailed characterization data for coal-derived liquids and other fossil-fuel-related materials. Chemical analysis is essential to the development of economically feasible technologies for efficient coal conversion and for the effective use of other sources of fossil energy. Mass spectrometry, either alone or when combined with chromatographic separation methods and especially when integrated with high-speed digital computer technology, constitutes a powerful and sensitive technique for acquiring the requisite analytical data. Characterization data are imperative for both developing and routinely monitoring commercial coal liquefaction processes as well as for the upgrading and refining of such fluids. Mass spectrometric characterization research will contribute to areas such as development of superior solvents in coal-liquefaction processes; catalyst development, deactivation, and regeneration; development of correlations to predict thermodynamic properties; determination of factors controlling the stability of coal-derived liquids; on-stream process monitoring; and identification and quantification of substances of environmental and biological concern.

RECENT WORK AND ACCOMPLISHMENTS – Fourteen industrial, governmental, and university laboratories currently involved in fossil-energy research were visited to assist in acquiring information for preparing a report on mass spectrometry and fossil energy conversion technology. Existing mass spectrometer facilities were augmented as follows. A commercial data acquisition and processing system was configured and interfaced to both the CEC 21-110B double-focusing mass spectrometer and the OSU IBM 370/158 computer. A comparator/microdensitometer was made manually operational. A digital integrator, an encapsulated sample injector, and a capillary sample splitting injector constitute acquired ancillary gas-chromatographic equipment. The combination field-ionization/electron-impact ion source was modified to operate in the field-desorption mode. Micromolecular probe distillation combined with field-ionization mass spectrometry (FI/MS) as a technique for extending the range of molecular weights analyzable was initiated by (1) interfacing a temperature-control module for the direct probe to the NOVA 3/12; (2) developing software for computer acquisition of both mass spectra and temperatures; and (3) implementing operation of the programs for processing the acquired ion intensities and temperatures. FI/MS, which produces virtually fragmention-free mass spectra, was previously shown in this program to be ideally suited to quantitative analysis of aromatic components of coal-derived liquids. Extension of the technique to the analysis of saturates would be significant because FI/MS would in contrast to electron-impact MS provide a molecular-ion-carbon-number group-type quantitative analysis of these fractions. The previously reported dependence of the relative sensitivities for FI of saturated hydrocarbons in the presence of low-molecular weight aromatic hydrocarbons on mixture composition suggested that such an extension might not be feasible. However, it was demonstrated that as the FI emitter temperature is increased from 100° to 270°C, the FI sensitivity for heptane relative to benzene decreases for any given binary mixture and exhibits a decreasing dependence on binary mixture composition. The relative sensitivity was found to be composition independent at an emitter temperature of 260°C. Similar results were then attained for a number of multicomponent mixtures containing a variety of saturated and aromatic hydrocarbons. Composition-independent FI sensitivities were also determined at 270°C emitter temperature for 20 alkanes and naphthenes in 22 mixtures containing only saturated hydrocarbons.

PLANS FOR THE COMING YEAR — Development of field-ionization mass spectrometry will continue as a technique for the quantitative analysis of saturates both in the absence and presence of aromatics. Both probe distillation/field-ionization mass spectrometry and field-desorption mass spectrometry will be applied to the analysis of high-molecular weight components from coal liquids and petroleums. Work will proceed with interfacing the comparator/microdensitometer to the NOVA 3/12 and developing the requisite software for computer requisition of mass spectra recorded on photoplates.

HEAT TRANSFER IN HIGH-TEMPERATURE FLUIDIZED BEDS WITH IMMERSED TUBES FOR COAL COMBUSTION SERVICE

OREGON STATE UNIVERSITY
DOE - $149,128; Oregon State U - $17,597
9/30/77 - 9/30/80
Principal Investigator - J.R. Welty

OBJECTIVES — This research deals with the heat transfer between a high-temperature (~1100°K) gas fluidized bed and immersed tubes. The first objective is to develop an analytical model that will predict the local heat-transfer rates and tube-surface temperatures as functions of bed-operating parameters. The second objective is to perform experiments with a high-temperature fluidized bed to provide data on local temperatures and heat-transfer coefficients around the surface of an immersed horizontal tube and to test the analytical model.

RECENT WORK AND ACCOMPLISHMENTS – The analytical model has been developed and tested by comparison with available experimental data. The only data found for these comparisons are at relatively low temperatures. Three curves were plotted to represent calculations and comparisons with the limited experimental results available. The first curve shows results for local heat-transfer coefficients (in terms of the dimensionless parameter, Nu) around the surface of a horizontal tube for a particle diameter of 2.8 mm and bed temperature of slightly over 300°K. The second curve plots the results using the same parameters as the first curve but with a bubble contacting the cylinder wall. The third curve presents the mean heat-transfer coefficient as a function of Reynolds number based on tube diameter. The present model's function is to relate these parameters.

The apparatus, which will achieve high-temperature experimental results for correlation and for model testing and validation, is nearly complete. A test bed capable of sustained operation at temperature of more than 1600°K has been constructed. The test section is 1 ft by 2 ft in cross section. Tubes can be inserted through the bed–along the 1 ft dimension–for measuring local and mean heat-transfer performance. Instrumentation is being developed to evaluate local heat flux, local temperatures, and the presence or absence of bubbles.

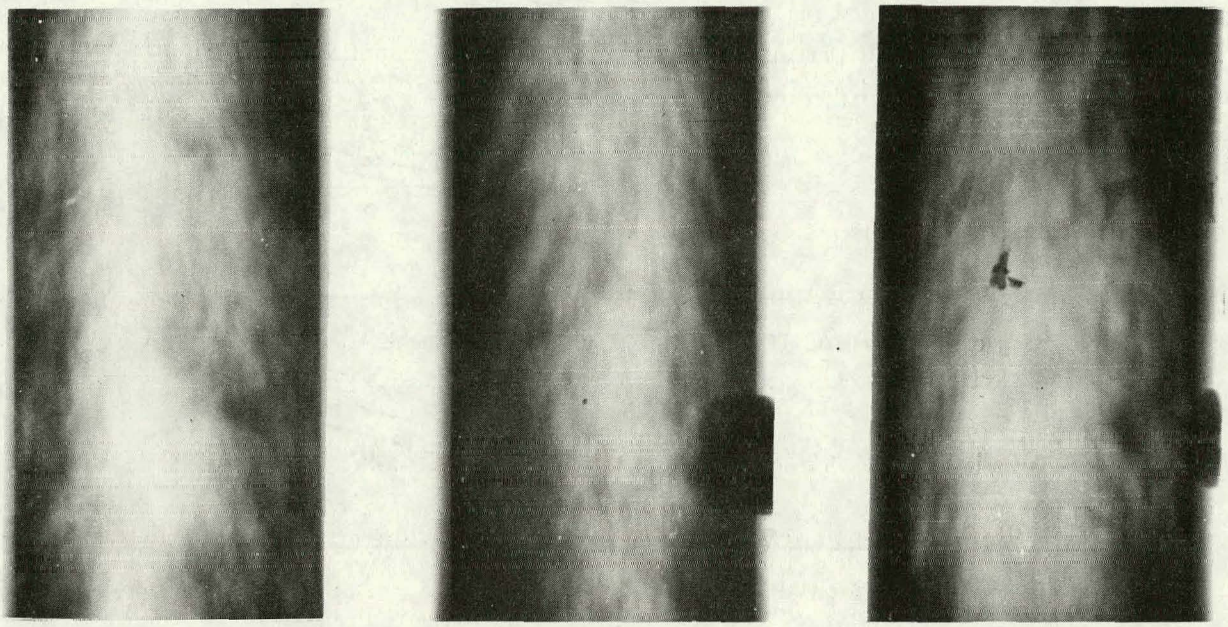
PLANS FOR THE COMING YEAR – The construction of the instrumented tube will be completed and tested in a hot bed environment, followed by extensive data gathering. Model comparisons and refinement will be performed continuously during the experimental program.

RECIRCULATING BED REACTORS FOR COAL PROCESSING

CARNEGIE-MELLON UNIVERSITY
DOE - $677,075; Carnegie-Mellon U - $35,636
7/1/76 - 9/30/78
Principal Investigators - T.W. Bierl, M.J. Massey

OBJECTIVES – This program intends to facilitate the application of recirculating bed reactors (RBR) to the processing of coal. An RBR is a device that continually circulates a portion of its solid inventory around a vertical loop. The driving force for solids circulation is the static head of solids in the reactor standleg, and the energy for solid transport is provided by the process fluid that contacts the solid inventory for reaction purposes. Task 1, "Coal Mixer Modelling Studies," involves the experimental investigation of the mass and heat-transfer problems associated with mixing streams containing entrained solids. A 3-in. diameter Plexiglas model of an RBR is being used for these studies. Task 2, "Coal Hydrodesulfurization Studies," has a process objective and only limited RBR hardware considerations. It is the goal of these studies to demonstrate significant organic sulfur reduction in coal by thermal processing in hydrogen and mapping the effect with variations in pressure, temperature, reactor residence time, and feed gas composition in a well-characterized experimental reactor. An experimental reactor called the hydrodesulfurization (HDS) flow reactor has been constructed for this purpose.

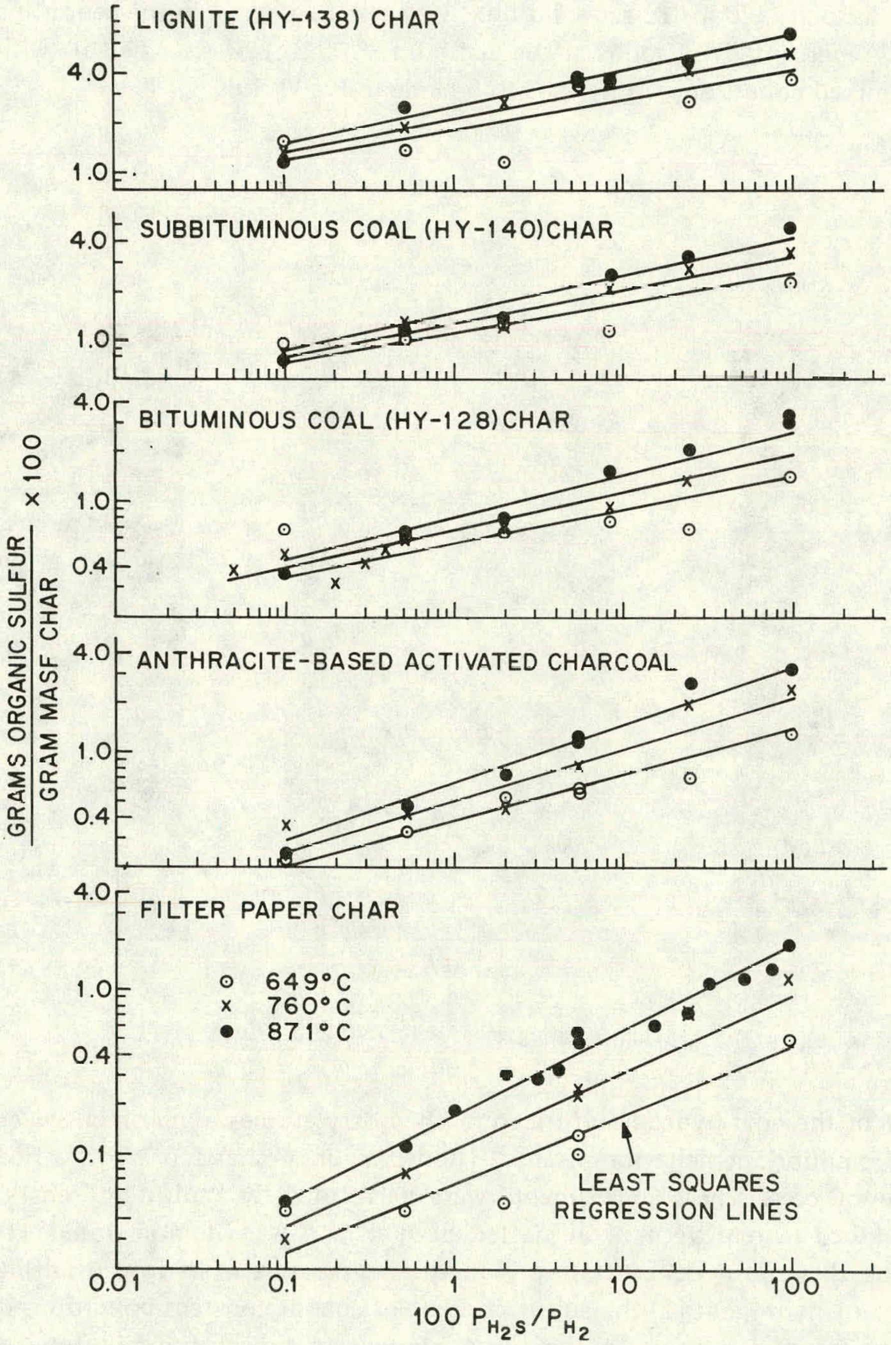
RECENT WORK AND ACCOMPLISHMENTS – As a prelude to mixing studies, the flow structure in the riser was determined. The phenomenon observed was characteristic of risers used for catalytic cracking in the petroleum industry. It can be described as a core/annulus flow structure, that is, a relatively high-velocity, low-density core surrounded by a high-density annulus. The existence of this phenomenon is confirmed by probe measurements and X-ray photographs. Mixing studies began with experiments in which solids were injected along the centerline of the riser. Dyed solids were used as the tracer. Injection at conditions similar to superficial riser-operating conditions (10.5 ft/sec-gas velocity, 20 lb/ft^2/sec-solid flux) gave rise to a decay in the centerline concentration from 100 to 15 percent dyed solids at the centerline in 2.3 ft of riser height, with a diameter of 3 in. The well-mixed condition corresponds to 6 percent dyed solids.



(a) Z = 2½ ft (b) Z = 9 ft (c) Z = 16½ ft

High Loading; High Velocity (15.5 ft/sec)

As a part of the coal hydrodesulfurization chemistry studies, experiments were performed to determine the equilibrium behavior of char. The behavior of char represents a boundary limit on desulfurization of coal. These experiments were performed by "sulfiding" chars that were previously acid washed to remove mineral matter. Several facts were demonstrated: (1) the functional group governing char sulfur concentration is the partial pressure of hydrogen sulfide divided by the partial pressure of hydrogen; (2) the sulfur content of char at constant conditions does not depend on the surface area of the char; (3) the sulfur content of the char is not time dependent from 10 min. to 32 hr; (4) the sulfur content of the char is reversibly changed by changing P_{H_2S}/P_{H_2}; and (5) the sulfur content of the char is dependent on the rank of the parent coal. Low-rank coals retain more sulfur at low values of P_{H_2S}/P_{H_2} than do higher rank materials. Although sulfidation and desulfurization are reversible, desulfurization has a time constant an order of magnitude (or more) higher than sulfidation. Also, the rate of desulfurization is apparently a function of pretreatment conditions. Operation of HDS flow reactor has not yet occurred because of mechanical or equipment problems. Most of these problems have been resolved.



Effect of Temperature Upon the Adsorption Isotherm

PLANS FOR THE COMING YEAR – Operation of the HDS flow reactor is expected, and a modest number of experiments will be completed. Further work on riser fluid mechanics and mixing is uncertain.

COAL GASIFICATION PROGRAM ENVIRONMENTAL ASSESSMENT

CARNEGIE-MELLON UNIVERSITY
DOE - $924,640; Carnegie-Mellon U - $36,007
7/76 - 7/18/79
Principal Investigators - J.P. Fillo, R.G. Luthy, M.J. Massey

OBJECTIVES — This program will develop the methodology and the data base necessary for an assessment of coal gasification processes environmental characteristics. Available resources of experimental data include bench-, PDU-, and pilot plant-scale systems encompassing five high-Btu and three low-Btu processes. Given this small subset of possible coal gasification processes and the inherent limitations of environmental analysis on small-scale plants, major operational objectives for the program are to define and focus primary efforts on the quantitative characterization of scalable sections of DOE-sponsored pilot plants and to relate measured environmental characteristics to specific operating conditions across all of the pilot plant facilities. Proper execution of these objectives will permit projection of demonstration- and commercial-scale environmental characteristics for these processes, enhance the scalability of the existing data, and ensure the applicability of program results to modified and/or new gasification processes.

RECENT WORK AND ACCOMPLISHMENTS — Four basic tasks comprise the efforts in this program: (1) strategic development of an effluent data base, (2) evaluation of process-related environmental engineering problems, (3) coordination of industrial hygiene sampling and analysis efforts, and (4) environmental assessment-support activities. Task activities have encompassed work with five high-Btu and low-Btu pilot plants. Strategic development of an effluent data base requires formulation of plant-specific environmental test plans, development/validation of methodologies for process stream sampling and sample preservation/analysis procedures, and monitoring individual pilot plant effluent characterization data bases. Activities in these areas include the development of a methods manual for coal gasification wastewater preservation and analysis, design and operation of a gas-sampling train for fast-response monitoring of raw process gas composition, and comprehensive analysis of both CO_2-Acceptor and HYGAS process raw data bases to uncover fundamental process variable/effluent production relationships.

Evaluation of process-related environmental engineering problems focuses on experimental verification of suspected gasification process variable/effluent production rates and the investigation of problems associated with potential effluent treatment strategies. Investigation of formation and decomposition of phenols and hydrocarbon condensates was conducted at both the bench- and PDU- scale jointly with the Pittsburgh Energy Technology Center (PETC). Probe studies of the CO_2-Acceptor gasifier's internal composition also provided evidence to further delineate these behavior patterns. The fact that pilot plant coal gasification facilities are not generally equipped with scalable effluent treatment equipment led to bench-scale studies of primary pretreatment and biological treatability of HYGAS and slagging fixed-bed gasifier wastewaters. Support studies also investigated the relevant kinetics of cyanide, thiocyanate, and sulfur chemistry in aqueous condensate. Coordination of industrial hygiene sampling and analysis efforts became an integral activity in the second year of the program. Activities coordinated in this program include toxics sampling, preservation, and analytical methods development/validation, and screening of selected process streams for evidence and severity of carcinogenicity and/or mutagenicity. Carnegie-Mellon University (CMU) will also provide support services on environmental issues relevant to DOE's gasification development program.

PLANS FOR THE COMING YEAR — Program efforts in all major task areas will continue. Effluent characterization efforts will occur at BIGAS, Combustion Engineering, and HYGAS facilities. Investigation of effluent treatment strategies will continue on both HYGAS and slagging fixed-bed gasifier wastewaters, the former with emphasis on tertiary treatment strategies to facilitate wastewater recycle/reuse. Joint PETC/CMU bench-scale phenolic compound decomposition studies will be completed. Industrial hygiene and effluent sampling efforts will be coordinated where possible to augment development of an environmental data base. Environmental data bases will be integrated across individual facilities in order to delineate the fates of various coal species occurring as effluents from coal gasification processing.

MECHANISMS OF THE HYDROGEN SULFIDE-DOLOMITE REACTION

CARNEGIE-MELLON UNIVERSITY
DOE - $231,259; CMU - $12,171
7/1/76 - 6/30/79
Principal Investigator - K. Li

OBJECTIVES — The program intends to establish the feasibility of using dolomite in cyclic sulfidation-regeneration operations for the removal of sulfur (as H_2S) in coal utilization processes and to determine the mechanisms of the basic reactions involved: half-calcination, sulfidation, and carbonation.

RECENT WORK AND ACCOMPLISHMENTS — The "second generation" thermogravimetric system, test-operated up to 1000°C and 70 atm, was completed and has been successfully used for 6 months. The major advantages of this new system are the substantial reduction in the duration of initial transient and in system volume, and a fivefold increase in the rate at which data can be collected. Kinetically, all the dolomites—Guelph, Stockbridge, Ledger, and Little Falls—behave quite similarly. The rate of half-calcination in a CO_2 atmosphere increases with temperature but is essentially independent of total pressure of CO_2 partial pressure. At temperatures above 760°C, the rate approximately doubles for every 40°C-temperature rise; at 1000°C, half calcination is complete within minutes, while it requires 15 to 30 min. to reach 50 percent conversion at 760°C. Based on the evidence of solid structure, half-calcination above 760°C appears to follow a mechanism closely parallel to that of the decomposition of austenite into ferrite and iron carbide, or the pearlite reaction. Except for conversion levels below 20 percent at 760°C, the conversion time data for all the dolomites can be correlated by the Avrami equation for a pearlite-type reaction. Sulfidation of half-calcined Guelph dolomite in a 1 percent H_2S/N_2 atmosphere occurs in two distinct modes depending on the temperature. At temperatures above 780°C, sulfidation involves two sequential steps: the formation of CaO from $CaCO_3$ followed by the reaction of CaO with H_2S. Each step proceeds topochemically with the $CaO/CaCO_3$ interface advancing ahead of the CaS/CaO interface. Below this temperature, H_2S reacts directly with $CaCO_3$ or the two interfaces proceed at the same rate. The MgO in the half-calcined dolomite reported to be inert during sulfidation by other investigators is found to react with H_2S. A kinetic model based on these observations and the assumption of the individual reaction being controlled by transport processes successfully predicts the dramatic increase of reaction rate with temperature, nearly linear increase with H_2S concentration, slight increase with flow rate, and decrease with pellet size. Recent data show that the reaction is slowed by CO_2 in the reacting gas, but enhanced by both H_2 and H_2O. Conversions of near 100 percent of CaS to $CaCO_3$ in $H_2O/CO_2/N_2$ mixtures within 1 hr were achieved at 750°C. In a 20 percent H_2O - 20 percent CO_2 - 60 percent N_2 mixture, the initial rate of carbonation decreases with temperature, while conversion after 1 hr first increases, reaches a maximum at about 750°C, and then decreases with increasing temperature. Conversion for a given reaction time always increases with increasing H_2O, CO_2, or both in the gas at all temperatures. At temperatures above 700°C, the reaction proceeds topochemically; below 700°C, however, sulfur remains uniformly distributed within the pellet even at 60 percent carbonation.

PLANS FOR THE COMING YEAR – Investigations into the effects of H_2 and H_20 on the sulfidation reaction will continue. The kinetic model for sulfidation will be further developed to include these and other effects such as the geographical origin of dolomite and the condition for half-calcination. More reaction rate and solid structural data on the carbonation of sulfided dolomite will be collected to provide additional information for the delineation of reaction mechanisms and for the formulation of a kinetic model for the carbonation reaction.

SOLID CIRCULATION AROUND A JET IN A FLUIDIZED-BED GASIFIER

LEHIGH UNIVERSITY
DOE - $100,000; Lehigh U - $18,960
9/1/78 - 8/31/80
Principal Investigator - H.S. Caram

OBJECTIVES – This project will study and measure particle and gas circulation around a jet at the bottom of a fluidized bed. The measurements will be made first in a transparent two-dimensional fluidized bed and later in a regular three-dimensional fluidized bed. In the first case, a "time of flight" laser anemometer system will be used whereas in the second case, a fiber optics probe is being studied. The results will be compared with those obtained using high-speed photography.

RECENT WORK AND ACCOMPLISHMENTS – The necessary equipment was acquired and a two-dimensional fluidized bed was designed and will be built.

PLANS FOR THE COMING YEAR – A laser and optical system, the photodetection system (photomultiplier), and the signal analyzer equipment will be purchased. The optical system will be mounted in an optical breadboard with the relatively small fluidized-bed system mounted in an X-Y-Z positioning system, which will be used to control the position of the optical fiber probe. An effort will be made to design the optical fiber probe with the critical studies being made with a rotating disc of particles. The light-scattering characteristics of the fluorescent particles as well as of the techniques needed to keep them in suspension will be studied. A high-speed video system will be used to check some of the results obtained as well as to get an overall picture of the flow characteristics.

METHANOL AND METHYL FUEL CATALYSIS

LEHIGH UNIVERSITY
DOE - $200,000
9/1/78 - 4/30/80
Principal Investigator - K. Klier

OBJECTIVES – The objective is to improve catalytic synthesis of methanol and methyl fuel by performing a kinetic study for optimization of the concentrations of oxidizing gases such as CO_2,

H_2O, and O_2 in the synthesis gas, and by improving existing catalysts through novel formulations based upon a detailed characterization of the catalyst microstructure. Specifically, this research program is aimed at: regulating the catalyst selectivity to C_1-C_4 alcohols through doping of the Cu-ZnO-Cr_2O_3 catalyst by low work function oxides, sulfides, and ion exchangers; improvement of thermal stability, sulfur resistance, and halogen resistance of the low-pressure catalyst through partial or total replacement of copper by other effective promoters; providing accurate kinetic data on the effects of oxidizing gases on methanol yields, catalyst selectivity, and its sulfur resistance; and investigating the potential of sulfide catalysts for low-alcohol synthesis.

RECENT WORK AND ACCOMPLISHMENTS – A series of catalysts was prepared based on binary Cu/ZnO = 30/70, previously found to be the most active low-pressure methanol synthesis catalyst, impregnated with Cs and Rb nitrates. In another series, Zr (IV) phosphates were exchanged (to 50 percent ion exchange capacity) with Cu(II). These catalysts are being tested for synthesis activity and selectivity to low alcohols. The binary Cu/ZnO catalysts were fully characterized by X-ray and electron diffraction, elemental analysis in the scanning transmission electron microscope, surface analysis in Auger and X-ray photoelectron spectrometers, surface area and pore distribution measurements, and optical absorption spectroscopy. The active phase was identified to the ZnO with dissolved cuprous ions that reaches the maximum activity at Cu/ZnO = 30/70 with 100 percent methanol in product, and the formation of this active phase was traced to the precursor compound $(Cu, Zn)_2\ (OH)_2CO_3$. It was further found that third components such as Al_2O_3 or Cr_2O_3 change the selectivity of the synthesis so that low alcohols or hydrocarbons are formed as minor side products.

PLANS FOR THE COMING YEAR – The Cu/ZnO = 30/70 catalyst will be tested for long-term performance, and the dependence of the conversion rate on the concentration of CO_2 in feed will be determined. Initial activity tests will be performed for the Cu/ZnO/Cs, Cu/ZnO/Rb, and Cu/Zr(IV)-phosphate catalysts. The best of these catalysts will be characterized for the same properties as the binary Cu/ZnO catalysts to find the causes of the formation of low alcohols. A water doser will be constructed as a part of a high-pressure flow reactor for the kinetic studies of the syntheses in the presence of water vapor at elevated pressures. Technical assessment of the feasibility of a low-pressure-low-alcohol synthesis process will be made.

CENTRIFUGAL FLUIDIZED COMBUSTION OF COAL

LEHIGH UNIVERSITY
DOE - $138,997; Lehigh U - $24,972
9/17/76 - 12/31/78
Principal Investigators - E. K. Levy, J. C. Chen

OBJECTIVES – Conventional fluidized-bed combustors (FBC), with the bed material fluidized against the force of gravity, have many desirable features; however, for large-capacity power-generation applications or with very fine bed material, these systems require extremely large distributor areas, causing difficulties with startup, solids feed, and bed mixing. The centrifugal fluidized bed (CFB) rotates about its axis of symmetry, and the fluidizing air flows radially inward through the porous cylindrical surface of the distributor. The inward drag force of the fluidizing air on the bed material is balanced by the large radial accelerations caused by the rotational motion, permitting much larger air flow rates per unit volume than are possible with a conventional fluidized bed operating against gravity. By varying the speed of rotation of the bed, flow rate of air, and bed temperature, it should be possible to achieve considerable variation in system power output providing the capability for operating over a wide range of part-load conditions. In addition, the added flexibility from bed rotation and the small size of the system should ease the problems of startup and solids feeding. With a bed material of dolomite or limestone to capture SO_2, the centrifugal combustor could be used to burn high-sulfur coal or coal char. Successful development of the CFB concept would provide a compact, clean, efficient system for coal or char combustion capable of operating at full- or part-load conditions. The system might be used for utility-size plants or for smaller industrial-power-generation applications. The objective is to determine the feasibility of operating a CFB in a continuous mode. The operating constraints as affected by limitations in fluidization, elutriation, and solids handling are to be determined.

RECENT WORK AND ACCOMPLISHMENTS — A series of experiments with an FBC model operated at room temperature and pressure, and fluidized-bed materials that simulated coal and coal char in specific gravity, particle size, and distribution were used to determine the requirements for minimum fluidization, bed pressure drop, and the extent of particle elutriation. The contraints affecting the addition and removal of material from the bed were determined. A second set of experiments was performed to study the fluid mechanics of the confined vortex flows that occur in the freeboard region of the CFB and to gather information on freeboard pressure drop. A 12-in.-diameter by 6-in.-high model was fabricated. Experiments showed that the ability to start a CFB from rest and achieve stable fluidized-bed operation depends critically on distributor design. Experiments were also performed to determine the influence of grid pressure drop, grid taper angle, angular velocity, particle size and density, and bed mass on bed pressure drop and minimum fluidization. Theoretical analyses, developed to predict the influence of these factors on system performance, are generally in good agreement with experimental observations. The rotational operation of the CFB leads to a vortex motion in the freeboard that tends to inhibit particle loss by elutriation. Experiments were performed to provide insight into the mechanisms for particle elutriation from a CFB, and the data are in good qualitative agreement with a terminal velocity model for particle loss. Test sections based on two different techniques for operating a CFB with continuous feed and removal were designed and fabricated. The data indicate that with these techniques, it is possible to feed and remove solids continuously and achieve a stable bed thickness in a rotating fluidized bed. Studies of the flow patterns in the freeboard region show that except for thin end-wall boundary layers and the core region at the axis of rotation, the flow is essentially inviscid and irrotational. Data obtained on pressure drop in the freeboard region are in qualitative agreement with results from a potential flow analysis.

PLANS FOR THE COMING YEAR — The project will be completed on December 31, 1978.

STEEL STUDIES FOR COAL GASIFICATION SYSTEMS

LEHIGH UNIVERSITY
DOE - \$294,920; Lehigh U - \$58,532
9/17/76 - 9/16/79
Principal Investigators - R.P. Wei, G.W. Simmons

OBJECTIVES — Steels used in coal gasification vessels and piping are exposed to mixtures of hydrogen, water vapor (steam), hydrogen sulfide, methane, carbon monoxide, carbon dioxide, and other gases over a wide range of temperatures and pressures. Such mixtures, under certain operating conditions, can either enhance or inhibit subcritical crack growth in these steels that could result from exposure to hydrogen and hydrogenous gases in these mixtures. Data are needed to aid in the establishment of design and operational guidelines for ensuring safe and reliable operation of coal gasification systems. The objective is to determine the correlation between the thermodynamics and kinetics of surface film formation and reduction in various gas mixtures and the kinetics of crack growth in these same mixtures such that a rational basis for predicting service performance of steels used in coal gasification systems can be established.

RECENT WORK AND ACCOMPLISHMENTS – Fatigue crack growth experiments have been carried out in vacuum, dehumidified argon, high-purity water vapor at 10 torr and high-purity hydrogen sulfide at 0.1 to 5 torr, principally at 300° and 400°K. Data obtained indicate that there is little or no influence of temperature on fatigue crack growth in these environments over the range of ΔK. Data obtained in vacuum are comparable to those obtained in dehumidified argon, and those obtained in high-purity water vapor are comparable to that obtained previously in air. Results obtained in high-purity hydrogen sulfide at 5 torr indicate that this gas is highly aggressive in enhancing crack growth and show that the environmental effect on crack growth is reduced at the higher temperature. The reduction in environmental effect is consistent with the previous results for hydrogen and with results on sustained load crack growth in hydrogen, water vapor, and hydrogen sulfide for other high-strength steels. The composition and extent of reaction of 2-1/4CR-1Mo steel in water vapor were determined at 300°, 400°, 500°, 600°, and 700°K. The reactions were carried out inside the Auger electron/X-ray photoelectron spectrometer. Exposures of the specimen to 5 torr water vapor for 2×10^3 sec at each temperature were made for ion-etched clean surfaces. Auger analysis indicated that only iron oxide was formed at each temperature; that is, no evidence was found for the preferential oxidation of either chromium or molybdenum. It was estimated that the oxide on 2-1/4Cr-1Mo steel after oxidation in 5 torr water vapor at 600° and 700°K is between 25- to 75-Å thick; after oxidation at 500°, 400°, and 300°K, the oxide is less than 25Å. The thickness of oxide produced by reactions with water vapor is much less than that formed in air or oxygen at comparable temperatures and pressures. The surface composition of 2-1/4CR-1Mo steel after exposure to 1000 torr hydrogen at 300°, 400°, 500°, 600°, and 700°K for 2×10^3 sec has been determined. The hydrogen exposures were made in a separate reaction chamber, and the specimens were transferred directly through a vacuum interlock into the spectrometer for analysis. Segregation of sulfur from the bulk to the surface was found to occur in increasing amounts with increasing temperatures. Comparisons of the rates of sulfur segregation in hydrogen and in ultra-high vacuum suggest that hydrogen enhances the rate of sulfur segregation in this steel. The significance of this result in view of the fact that the rate of fatigue crack growth of 2-1/4Cr-1Mo steel decreases for increasing temperature is being considered.

PLANS FOR THE COMING YEAR – The experimental phases of the program will be continued, including the establishment and confirmation of conditions (primarily ratios of partial pressures and temperatures) for surface film formation and reduction in H_2O/H_2 and H_2S/H_2 mixtures, as predicted by available thermodynamic data; and determination of whether the susceptibility to crack growth and the kinetics for crack growth in hydrogen that is present in these mixtures are altered by changing conditions from that for surface film formation to that for film reduction as defined by the aforementioned surface chemistry experiments.

MINERAL MATTER DISTRIBUTION IN PULVERIZED FUEL COALS

PENNSYLVANIA STATE UNIVERSITY
DOE - \$192,431; Pennsylvania State U - \$10,129
4/76 - 3/79
Principal Investigators - L.G. Austin, R. Essenhigh, E.W. White

OBJECTIVES – The object is to study the correlation of the mineral matter of pulverized coal (PC) fuel with slag deposit formation in the upper regions of utility boiler furnaces.

RECENT WORK AND ACCOMPLISHMENTS – A computerized SEM has been developed for the approximate quantitative analysis of the elements Fe, S, Al, Si, Ca, and K in each coal particle of several hundred particles representative of the total PC. A suitable mounting medium consisting of barium methacrylate, paraplex, and epoxy resin has been developed to enable coal particles mounted in this matrix to be distinguished from the matrix by the SEM beam. Size fractions of coal obtained using micromesh sieves are dispersed in the medium and a polished slide prepared. The beam is told to examine only imbedded particles having a diameter within the original size range, thus eliminating smaller fragments of coal produced by the polishing. Tests on particles of known minerals, such as FeS_2 and $Si0_2$, have shown that the SEM X-ray counts from many particles are within reasonable standard deviations of a mean. Similar SEM tests have been performed on slides of dispersed particles (without mounting and polishing), and in this case the standard deviation of counts is too wide for accurate measurement. The beam recognizes a coal particle, traces and records its perimeter, calculates a mean diameter, and chooses test points for X-ray counting. A rapid version of the Colby program for quantitative analysis has been implemented for on-line analysis. Preliminary results have shown a wide range of types and quantities of mineral matter between particles. An apparatus has been developed for studying the adhesion of droplets of slag to a cooled substrate. A pellet of coal ash (or ground-up mineral matter) is formed on the end of a Pt wire and heated in a small oxygen-methane fired furnace until it melts and falls off the wire. The molten droplet falls 3 cm onto a substrate of closely controlled temperature. It has been found that if the temperature is less than a "sticking temperature," T_s, it will not form an adherent solid droplet; if the substrate temperature is greater than T_s, the droplet does adhere. The higher the substrate temperature, the higher the force of adhesion. Ash droplets from four coals were tested on an oxidized mild steel substrate temperature of 600^oC varying from 430^o to 500^oC, and adhesion strengths at a substrate temperature of 600^oC varying from $50 gcm^{-2}$ to $5000 gcm^{-2}$. High-speed photography shows that the droplet is molten when it strikes the substrate, but the contact region freezes within 1 to 2 milliseconds and the frozen region spreads up the drop. On an oxidized mild steel substrate, this initial time appears to be sufficient to form enrichment of iron on the contact regions. When the droplet is sheared off, it is the oxide layer that breaks from the substrate. A coating of alkali on the substrate greatly reduces the sticking temperature. A vertical plane flame furnace with a capacity of 10 to 20 lb/hr of pulverized coal has been tested as a simple, closely controllable analog of the burning and melting history of particles in a boiler furnace. Water-cooled probes have been constructed to test whether the concept of sticking temperature found in the laboratory tests can also be applied in this furnace. The original furnace design was unsatisfactory because of low flame temperature, incomplete combustion, and too high exit gas temperatures. The furnace has been modified by adding 4 ft of length and is now operating satisfactorily. A long-range optical system has been installed to view the initiation of deposit on a selected area of the probe.

PLANS FOR THE COMING YEAR — Work will involve the systematic description of the different types of particle-mineral matter in PC for a range of coals. The adhesion behavior of representative mineral compositions will be studied under a variety of conditions. Coupons of substrate steels will be exposed in the plane flame furnace at gas temperatures comparable to those in boiler plants, at substrate temperatures corresponding to water-tube surface. The coupons will be removed for testing in the adhesion apparatus, to see if deposited films of volatile chemicals are leading to strong adherence of the types of mineral combinations detected in the PC.

FRACTURE OF REFRACTORY CONCRETES

PENNSYLVANIA STATE UNIVERSITY
DOE - $108,328
6/1/77 - 5/31/80
Principal Investigator - R.C. Bradt

OBJECTIVES — The objectives are to investigate and understand the fracture characteristics of refractory concretes (castables) of the types under consideration as candidates for coal gasifier linings. These objectives will be pursued by experimentally measuring the mechanical properties and fracture mechanics parameters necessary for coal gasifier design with refractory concrete linings.

RECENT WORK AND ACCOMPLISHMENTS — Measurements of elastic moduli, modulus of rupture, work of fracture, and the fracture toughness of a series of refractory concretes have been made from room temperature to 1200°C. The refractory concretes are combinations of the different commercial aggregates Mulcoa 47, Mulcoa 60, and a Tabular Alumina T-61 with the commercial calcium aluminate cements Secar-250, Refcon, and CA-25. Actual concretes consist of a specific generic aggregate distribution (75 percent) and the respective cements (25 percent). In addition, the same mechanical property data have been generated for two lightweight insulating refractory concretes—Cerlite and Litecast. The relationships of the aforementioned properties to the specific cements, aggregates, and bonding characteristics (for example, the loss of the hydraulic bonds) have been observed also. The importance of measuring these mechanical properties at the elevated temperatures of interest, rather than at room temperature as has been done, is illustrated by this result of fracture toughness variation: a particular concrete—Mulcoa 47/Refcon—the fracture toughness difference is more than a factor of 2.

PLANS FOR THE COMING YEAR — Measurements will continue on the generic concretes and insulating castables. Specific aggregate distributions to improve strength and fracture characteristics will be investigated. The interaction of cracks with aggregates and propagation through the cement bonds will be monitored by acoustic emission.

ALIPHATIC COMPONENTS OF COAL

PENNSYLVANIA STATE UNIVERSITY
DOE - $85,000; Pennsylvania State U - $4474
9/1/78 - 8/31/80
Principal Investigator - N. Deno

OBJECTIVES — A new method has been discovered for elucidating the chemical structure of coal, consisting of oxidatively degrading the coal with H_2O_2—CF_3COOH-H_2SO_4. The aromatic components are destroyed and the aliphatic components preserved. This technique is judged to be the best method for elucidating the aliphatic part of the chemical structure of coal and is being applied to coals selected for varying ease of liquefaction, rank, and geological age and geographical area. It is also being applied to coal before and after liquefaction.

RECENT WORK AND ACCOMPLISHMENTS – Data are being accumulated on 50 coal samples selected and supplied by Mobil Oil Company and the College of Mineral Industries at Penn State. Also under study are 20 samples of liquids and residue from coal liquefaction. It would be inefficient and speculative to attempt a detailed analysis at this time; however, only 20 products were obtained from Illinois No. 6 Monterey coal and 8 products accounted for 90 percent of the total weight. It is concluded that coals are relatively uniform in structure and that the concept of extensive chemical changes with geological time is incompatible with the simplicity of products. Different coals give different products and possess different chemical structures.

PLANS FOR THE COMING YEAR – The program will be continued. It is expected that the results will provide definitive knowledge regarding the chemical structure of coal.

PERFORMANCE EVALUATION OF AUTOMATED EXTRACTION SYSTEM

PENNSYLVANIA STATE UNIVERSITY
DOE - $165,251
6/17/77 - 2/28/79
Principal Investigators - R.L. Frantz, R.H. King

OBJECTIVES – This project is a part of DOE's Automated Remote Controlled Continuous Miner (ARCCM) research program. The objective is to perform an independent, comprehensive engineering documentation of the in-mine trial of a prototype mining system that was proposed to increase production in underground coal mines. Through the documentation of the machine's performance, the Audit Team is to assist in the evolvement of the prototype, and recommend improvements to the system as well as operating, maintenance, and training plans. The machine, built by the National Mine Service Company (NMSC), is called the Automated Extraction System (AES). It underwent a field trial at the Consolidation Coal Company's (Consol) McElroy Mine beginning in late August 1977, and concluded in May 1978, with intervening periods of machine modification and the UMWA strike. In the prototype AES, the normal face activities of cutting and loading were combined with on-board roof support (temporary and permanent), ventilation, environmental controls, and a semiautomatic cutting cycle. The idea of combining these functions originated with Consol's Lee Engineering Division. NMSC was the successful bidder on a cost-sharing contract with the U.S. Bureau of Mines. Initial claims made by NMSC were that the AES would be a highly reliable and easily maintainable machine.

RECENT WORK AND ACCOMPLISHMENTS – A data collection and analysis plan was developed by the Audit Team to evaluate AES performance based on five criteria: safety, production, performance, economics and human factors. It consisted of a full-time audit (observations and time and motion studies) of the AES, a worker opinion questionnaire, and several special audits (general safety, roof support and strata control, centerline maintainability, canopy protection, ventilation, lighting, noise, bolting-platform stability, crosscut turning, cleanup, and dilution of the coal with rock). Quantitative data were emphasized but qualitative data were also necessary especially to account for human factors. The following in-mine trial periods were documented with personnel in the mine during every shift: First Production Period—August 30 through October 20, 1977; Modification Period—October 20 through December 6, 1977, and April 5 through April 11, 1978 (AES modified to alleviate some design and geologic problems); Strike Period—December 7 through April 4, 1978 (AES idled by UMWA contract strike); Second Production Period—April 12 through May 24, 1978; and Disassembly Period—May 25 through September 2, 1978 (AES removed from McElroy Mine). After the trial, NMSC and Consol cited problem areas encountered with the AES, in an interim report submitted to the DOE in September 1978.

PLANS FOR THE COMING YEAR — The final report is expected to be completed by February 1979. It will provide a workable data base for the development of future machines in the ARCCM research effort. The roof, floor, and coal strata at the McElroy Mine test site will also be examined to determine the effect of the strata on the operation of the AES and the effect of the AES on the mine strata. That report should be completed in March 1979.

TRANSITION METAL CLUSTER COMPLEXES AS CATALYSTS

PENNSYLVANIA STATE UNIVERSITY
DOE - $40,000; Pennsylvania State U - $11,282
9/1/77 - 8/31/79
Principal Investigator - G.L. Geoffroy

OBJECTIVES — The goal is to develop selective and efficient catalysts for the conversion of coal-derived synthesis gas into useful organic feedstocks and fuels. The specific objectives are to conduct a thorough evaluation of a variety of metal clusters for their ability to catalyze reduction of CO, to optimize the reaction conditions for these clusters identified as catalysts, and to develop a thorough understanding of the interactions of CO and H_2 on transition metal clusters.

RECENT WORK AND ACCOMPLISHMENTS — Initial efforts have been devoted to establishing the reaction conditions and analytical procedures necessary to evaluate the ability of specific metal carbonyl clusters to catalyze reduction of CO. The first level of evaluation involves heating 3×10^{-3} M isooctane solutions of each cluster to 100°C under 1 atmosphere pressure of a $3/1\text{-}H_2/CO$ gas mixture. The gases above the samples are periodically analyzed by gas chromatography to determine if any hydrocarbons or CH_3OH have been produced. The following clusters were found to decompose under these conditions and no organics were detected: $Fe_3(CO)_{12}$, $H_2FeRu_3(CO)_{13}$, $CHoRu_3(CO)_{13}$, $CH_3CCo_3(CO)_9$, and $PhCCo_3(CO)_9$. $H_4Ru_4(CO)_{12}$ appeared stable under these conditions but no organics were produced. A reactor system has been assembled that will permit a study of carbonyl clusters supported on SiO_2 and Al_2O_3 as heterogeneous catalysts for CO reduction. The objective is to avoid the high temperatures (400° to 500°C) generally used in the preparation of reduced metal catalysts and hence avoid the sintering which accompanies the reduction. Since the clusters are already in the zero valent state and contain the substrate molecules CO and H_2, such high-temperature reduction is not necessary. The temperature for each supported cluster will be slowly raised under a $3/1\text{-}H_2/CO$ atmosphere to allow observations of when the CO reduction begins to occur and the distribution of products formed. By beginning with well-defined metal cluster and especially mixed-metal cluster (e.g., $H_2FeRu_3(CO)_{13}$) precursors, it should be possible to study the effect of particle size at the lower limits and metal-composition on CO reduction. Thus far, only $Ru_3(CO)_{12}$ supported on SiO_2 has been examined. When preheated to

200° or 250°C under an H_2 atmosphere and then placed under CO/H_2, methane and C_2 and C_3 hydrocarbons are produced. The catalyst activity decreases over a period of hours but may be regenerated by heating under H_2. No activity is observed at temperatures below 200°C.

PLANS FOR THE COMING YEAR – The following clusters will be examined for their ability to homogeneously catalyze CO reduction: $Ru_3(CO)_{12}$ $CO_4(CO)_{12}$, $Rh_4(CO)_{12}$, $H_3Re_3(CO)_{12}$, $H_3Mn_3(CO)_{12}$ $HFeCo_3(CO)_{12}$, $H_4Os_4(CO)_{12}$, $Fe_5C(CO)_{15}$, and $Fe_6C(CO)_{16}{}^{2-}$. Other clusters will be evaluated as they become available. Once clusters are found that catalyze the reaction, the conditions will be optimized and the selectivities of the catalysts determined. A program is also being initiated to model the various steps that might occur during CO reduction on a metal surface by studying the reactivity of appropriately designed or selected metal clusters.

RELATION OF COAL CHARACTERISTICS TO LIQUEFACTION BEHAVIOR

PENNSYLVANIA STATE UNIVERSITY
DOE - \$1,005,537; Pennsylvania State U - \$45,882
7/1/76 - 4/30/79
Principal Investigator - P.H. Given

OBJECTIVES – The objective is to ascertain how the yield and composition of liquefaction products are determined by the rank, geological history, petrography, mineral distribution, and so forth of the feed coal, the findings to be expressed quantitatively to the extent possible. Experience in the operation of pilot plants has focused attention on certain aspects of this program as particularly important, such as the dependence of product distillability on coal characteristics (since filtration has proved difficult), and the variability of mineral catalysis (since such catalysis is proving important in promising processes under development).

RECENT WORK AND ACCOMPLISHMENTS – An experiment was completed in which duplicate runs on 104 coals from three important geological provinces were performed in small batch reactors under standard conditions using tetralin only. It was found necessary to carry out a cluster analysis on the set of samples before valid multiple regression analyses could be performed on the data. The sample set was partitioned into three groups, characterized as of medium sulfur content, high rank (mostly HVA) - Group 1; high sulfur, medium rank (mostly HVB, some HVA and HVC) - Group 2; and low sulfur, low-to-medium rank (HVC and HVB) - Group 3. The mean levels of conversion for the groups were: Group 2 > Group 3 > Group 1. Group 3 coals were mostly from the Rocky Mountain province, and Group 1 from the Eastern or Appalachian province; Group 2, however, contained a mixture of Interior (Illinois) and Eastern coals. Regression equations for the three groups separately called out a different set of coal properties in each case for correlation with conversion. A set of data became available from Gulf R&D Company, using a 1 kg/hr continuous-flow reactor pressurized with hydrogen, showing that the separation of conversion levels for Group 1 and 2 coals was even greater than in the batch reactor data. Kinetic analysis of the loss of oxygen and functional forms of oxygen from a coal indicated that splitting of ethers is an important process in the early stages of liquefaction with tetralin. A new method of analyzing the temperature coefficients of liquefaction was set up that recognizes the process must proceed by a large number of components reacting in parallel (simultaneously). Application of the method to data for three coals showed that apparent activation energies change with the level of conversion, the magnitude of the change being different for the three coals studied. Petrographic analysis of the solid residues from batch liquefaction runs performed under different conditions of temperature, residence time, and agitation rate shows that the particles in a sample of one coal exhibit a surprising heterogeneity of behavior, even different particles of the same maceral. Attempts to measure the rate of diffusion of donor solvent to the loci of thermal decompositions inside coal particles have been limited to low temperatures (up to 70°C). Nevertheless, it has been possible to infer that diffusion by imbibition or surface transport is likely to be rapid with low rank coals (sbb A and HVC) at 350° to 400°C. Even hydrocarbons can cause swelling of coals. Studies of the inorganic matter in five lignites has shown that up to about 50 percent of the ash-forming constituents may be bound to organic matter by ion exchange with carboxyl groups or by chelation. The organic matter and organic processes in the original peat swamps evidently have a profound effect in determining what inorganic species become associated with the peat and derived coals.

PLANS FOR THE COMING YEAR — A study will be made to determine how the correlations of coal conversion, outlined above, are perturbed when hydrogen is present as well as donor solvent. When the full set of data from the Gulf experiments (with 60 coals from the PSU sample base) are available, it will be examined statistically to test the significance under the Gulf conditions of the classification achieved by cluster analysis. Various regressions will be developed between liquefaction behavior, especially conversion and distillability, and coal characteristics. The variability of catalysis by coal minerals will be examined in more detail, as will the phenomenology of liquefaction as revealed by petrographic analysis of solid residues. Data will be generated on the dependence of the composition of coal liquids on the characteristics of the feedstock.

INSTRUMENTAL ANALYSIS OF SULFUR COMPOUNDS IN COAL PROCESS STREAMS

PENNSYLVANIA STATE UNIVERSITY
DOE - $136,397; Pennsylvania State U - $8000
9/30/77 - 9/29/79
Principal Investigator - J. Jordan

OBJECTIVES — A comprehensive, versatile, and dependable capability will be developed for the quantitative determination of sulfur contaminants in coal-conversion process streams. A combination of specially selected electrochemical and thermochemical methods of analysis will be used that have sufficient sensitivity for monitoring trace concentrations at even the most stringent tolerance threshold levels.

RECENT WORK AND ACCOMPLISHMENTS — Through the use of thermodynamic data, expected "abundance profiles" of sulfur compounds have been delineated as a function of two readily measurable experimental parameters—redox potential and pH. Inorganic and organic sulfur compounds have been determined by differential pulse voltammetry at a rotated glassy carbon indicator electrode. Advantage was taken of the electroreduction of sulfur dioxide (to elementary sulfur and water), which proceeded with 100 percent current efficiency in aqueous hydrochloric acid in a relatively narrow range of potentials. The applicability of the method extended from 0.5 to 100 ppm of sulfur dioxide, which compares with a low limit of 4 ppm in Synthane coal gasification process streams. The precision and accuracy attained were 1 percent. The following contaminants known to occur in Synthane effluents (at ppm levels specified between parentheses) were found *not* to interfere with the method: phenol (200 to 7000), thiocyanate (20 to 1000), ammonia (2500 to 11000), chloride (30 to 500), and sulfate (1400). On the other hand, dibenzothiophene (a known organic sulfur contaminant) was successfully detected qualitatively and determined quantitatively in products of a coal liquefaction process by measuring the faradaic current signals resulting from the electrooxidation of dibenzothiophene to the 9-[3-dibenzothiophenyl]dibenzothiophenium ion. Concomitantly, a general approach of enthalpimetric analysis has been developed for the determination of several sulfur compounds (e.g., sulfide, sulfite, thiosulfate, sulfate) by measuring, in an adiabatic cell, the heats evolved in appropriate acid-base, oxidation-reduction, complexation, and precipitation reactions. Simultaneous reliance on a voltammetric and an enthalpimetric technique for each contaminant is expected to provide virtually "fail-safe" reliability, because the two types of methodologies are unlikely to be subject to similar systematic errors.

PLANS FOR THE COMING YEAR – A manual of "analytical resources for the determination of sulfur compounds by instrumental methods" will be developed for facilitating in-plant monitoring of coal-conversion process streams. It will include appropriate computer programs for predicting (on the basis of thermodynamic data) expected concentrations of various significant moieties; precise, accurate, and convenient procedures for the quantitative determination of each and every important sulfur contaminant by two independent methods. Coverage will encompass all consequential inorganic sulfur moieties, as well as organic contaminants such as thiophene and furan.

EVALUATION OF OPERATIONAL CONSTRAINTS IN CONTINUOUS-MINING SYSTEMS

PENNSYLVANIA STATE UNIVERSITY
DOE - $174,787; Pennsylvania State U - $13,325
7/1/75 - 7/1/79
Principal Investigators - C.B. Manula, S. Suboleski

OBJECTIVES – Both simulation and field data are being used to analyze the relationships between productivity and the physical and systems components of mining so that the objectivity and accuracy of production forecasts may be improved. The purpose is twofold: to analyze the application of new and novel systems for underground coal mines that use continuous mining equipment, and to determine the effect of physical variables on productivity in milling-type continuous-miner sections. The feasibility assessment of new equipment is designed to demonstrate potential improvements in productivity, evaluate costs for alternative systems, and indicate possible modifications to existing systems. The study of independent physical variables—seam height, depth, and hardness; roof and bottom quality; and water and grade conditions—will determine their effect on production and lead to a methodology for predicting productivity under varying mining conditions.

RECENT WORK AND ACCOMPLISHMENTS – A series of systems analyses have been made using time and performance data obtained from a mine systems model—the PSU/USBM Underground Materials Handling Simulator (UGMHS). These analyses determined the relatioship between face lengths and productivity for a shortwall mining system and shortwall panel; assessed the production lost through intermittent shuttle-car haulage; and determined production for various continuous-miner systems using both place changing and miner-bolters. Alternative mine plans and systems were evaluated to predict variations in productivity, and a minimum cost system was selected. Simulation studies have been carried out to analyze several new mine system components. An evaluation of an Automated Extraction System indicated that planking would be a significant deterrent to high productivity, and showed the effect on productivity of different types and lengths of bolts for various cut plans. This system combined with continuous haulage could be expected to raise production and provide an attractive rate of return. It was determined that the rate of return on a new Temporary Roof Support System would be attractive, but that the production gain would not be as great as predicted. A Hopper-Feeder-Spillage-Cleaner was found to increase production by as much as 15 percent, and cost analyses of a Belt Extender System showed the conditions under which this would be a valuable component of a continuous-mining system. An Auto-Track Bridge Conveyor Train was compared with a standard Mobile Bridge Conveyor and showed potential as an alternative investment. The economics of a steam-powered face haulage vehicle compared favorably with conventional shuttle cars, provided that the manufacturer's claim of a 40 percent increase in capacity over standard units coupled with a 0.1-min. turn-car time and 0.35-min. discharge time can be attained. This assessment assumed identical reliability in the two systems. UGMHS was used in simulation studies of the physical variables in mines to determine the underlying relationships between the variables and production. Field data compiled from over 400 operating sections in the Eastern U.S. was subjected to empirical analysis and compared with the simulation results, which led to the development of a series of simple equations that can be used to predict productivity for new mines in virgin areas or projected sections of existing mines. The equations use drill information to obtain the physical variables along with systems information determined by the user, and should prove to be a useful tool for mine planning. A mathematical model for simulating the behavior of a longwall coal production system was requested by Pittsburgh Mining Technology Center. This simulator incorporated both deterministic and stochastic methods to calculate the size and density of support; the cutting force, power requirements, and haulage speed for the loader -shearer; the conveyor size, speed, and power requirements; and the delay generation at the head, tailgates, and face.

PLANS FOR THE COMING YEAR – UGMHS will be adapted for use on a UNIVAC 1108/1110 system, and the rail-haul subassembly will be updated and made an integral part of the model. Concurrently, the user's manual of UGMHS will be revised extensively to reflect recent modifications in the simulator and new applications for retreat mining that have been suggested by FMC. Work will continue on the assessment of new and novel equipment, specifically simulation studies to obtain the duty cycles of battery-powered shuttle-car systems. These results will determine the effect of various battery designs on shuttle-car performance. The model will be put into an interactive mode, which would allow the user to make *a priori* adjustments as the simulation takes place.

SiC, Si_3N_4, Si_2N_20, AND SIALON STABILITY IN COAL GASIFICATION ENVIRONMENTS

PENNSYLVANIA STATE UNIVERSITY
DOE - $202,779
9/1/77 - 8/31/80
Principal Investigator - A. Muan

OBJECTIVES – This research is aimed at determining and evaluating stability relations of SiC, Si_3N_4, Si_2N_20, and Sialon as a function of gas compositions in the temperature range of 1000° to 1600°C, and ascertaining the effects and rates of slag attack on them. The data obtained will establish maximum temperatures for use of commercial SiC refractories in coal gasifier environments, which will provide an improved basis for making sound recommendations regarding the proper choice of refractory materials and design parameters in full-scale coal gasifiers.

RECENT WORK AND ACCOMPLISHMENTS — Previous stability data among phases in the systems Si-C-0, Si-N-0, and Si-Al-N-0 have been largely confirmed by evaluations carried out here. It is concluded that the carbide-, nitride-, and oxynitride phases in general will be subject to severe oxidation reactions in the slagging gasifier environment, and that the extent and nature of the ersion of these bodies will be largely determined by the degree of compatibility between the slag and the oxidation layer formed on the refractory, and the rate of attack of the slag on this oxidation product. It has been demonstrated clearly that Fe0 as a constituent of the slag has a very deleterious effect on SiC. Furthermore, it has been shown that reaction between SiC and Fe0-containing slags has associated with it precipitation of metallic iron at or near the SiC/slag interface, observed both in reacted samples of commercial brick exposed to slag attack and in reactions between SiC and synthesized slags.

PLANS FOR THE COMING YEAR — The experiments carried out so far have shown that protection against reaction between SiC and Fe0-containing coal-ash slags is dependent on the preservation of a $Si0_2$- or silicate layer on the carbide. Hence, a slag having constituents reacting with $Si0_2$ or the solid silicate to remove this layer would have a strong detrimental effect on the ability of the SiC body to withstand corrosion by oxidation. It is clear that the rate and mechanism by which the protective $Si0_2$ layer is removed by reaction with the slag will be a critical factor in evaluating behavior of SiC refractories in a coal gasification environment. Research thus will be directed primarily toward providing the necessary data base and insight into this process.

REFRACTORY EROSION IN COAL GASIFICATION AND COMBUSTION SYSTEMS

PENNSYLVANIA STATE UNIVERSITY
DOE - \$40,000; Pennsylvania State U - \$2100
9/1/77 - 8/31/79
Principal Investigator - H.E. Shull

OBJECTIVES — Two complementary tasks are being conducted to gain understanding of the high-temperature erosion resistance of alumina refractories in coal gasification and advanced coal-combustion environments. With experimental data on the erosion behavior of two selected aluminas under jet impingement conditions as a function of temperature and of impinging particle size, velocity, strength (hardness), and direction, the best existing theory of the erosion of brittle materials will be tested. Simultaneously, a study of these same erosive particles and refractory target materials is to be carried out having more general application to the solid-particle erosion problem; namely, an investigation of the potential of laser holography as a means of studying single-particle impacts in their various stages. The use of the pulsed holographic method is also to provide the particle-impact velocity data needed for the first task.

RECENT WORK AND ACCOMPLISHMENTS — Work on this project has been discontinued temporarily so that alternative staffing arrangements can be implemented. There have been no significant accomplishments.

PLANS FOR THE COMING YEAR — A request for a 2-year, no-cost extension has been submitted. The experiments in the initial year of extension will be limited to testing of erosion resistance of alumina refractories at room temperature, while the design and construction of an appropriate furnace system are being carried out. Target materials will be prepared and subjected to jet impingement erosion designed to simulate the low-particle concentration/high-particle end of the spectrum of operating conditions found in typical gasifiers and advanced coal-combustion systems. Detailed investigations will be made of the size and shape of the spent erosive particles, of target debris, and of the worn target surfaces. Pulsed laser holography will be evaluated as a method of measuring particle velocities, and used as such when possible. Efforts will be applied also to develop holography as a practical tool for examining single-particle impacts.

CHARACTERISTICS OF AMERICAN COALS IN CONVERSION INTO CLEAN ENERGY FUELS

PENNSYLVANIA STATE UNIVERSITY
DOE - $3,220,894; Pennsylvania State U - $345,633
6/26/75 - 8/25/79
Principal Investigator - W. Spackman

OBJECTIVES — The goal is the prediction of the response of coal in beneficiation, gasification, and combustion processes. Specific objectives of the program include the detailed characterization of a broad spectrum of the nation's major coal reserves; investigation of coal property interrelationships; investigation of the preparation characteristics of U.S. coals and of the feasibility of manipulating coal composition for conversion processes; design, construction, evaluation, and use of bench-scale reactors and reactivity tests; development of an understanding of the factors that affect the structure of chars produced by the thermal treatment of coals of varying rank and relating variability in char structure to char reactivity in different atmospheres; and determination of the requirements for the use of low-volatile coals and chars in pulverized coal boilers.

RECENT WORK AND ACCOMPLISHMENTS — This year 184 coal samples were obtained, bringing the total number of samples collected in the course of the program to 786. A wide range of analytical procedures have been used to characterize the samples, including mineralogical analyses of the low-temperature ash using a combination of X-ray diffraction, infrared, and chemical analyses. Cluster analysis of a part of the data base indicates that four major natural groupings can be distinguished on the basis of rank, petrographic composition, and organic sulfur content. Changing from a continuous-scanning mode to a step scan has improved the resolution of the rapid scan system of automated reflectance microscopy. Work in gasification includes the following studies: kinetics of volatile matter release from lignites under conditions of rapid heating and short contact times; characterization of microporous chars by small angle X-ray scattering (SAXS); effect of preoxidation of caking coals on their volume changes during subsequent heating; catalysis of lignite char gasification by various exchanged cations—dependence of activity on reactive atmosphere; relation of active surface area of chars to their reactivity; and measurement of exchanged cations on American lignites. Significant accomplishments in these studies are: enhancement of reactivity of chars produced from caking coals by their preoxidation; demonstration of the feasibility of using SAXS to measure the total surface area and structural parameters of chars; development of a reliable measurement system to quantitatively follow swelling of caking coals; and measurement of the kinetics of volatile matter release from lignite as a function of temperature, time, and particle size.

PLANS FOR THE COMING YEAR – All coal samples will have been subjected to basic characterization including emission spectrometry on the high-temperature ashes for major, minor, and some trace elements. A technique for performing carbon, hydrogen, and nitrogen more accurately and as reliably as the standard techniques is being investigated. Research will continue in the areas discussed except for the study on effects of preoxidation of caking coals. A high-pressure, laminar-flow isothermal reactor will be housed in a new high-pressure facility and fully commissioned before starting pyrolysis studies.

OXIDATIVE PRETREATMENT OF COAL

UNIVERSITY OF PENNSYLVANIA
DOE - $127,925; Pennsylvania U - $6207
7/1/77 - 6/30/78
Principal Investigator - D.D. Perlmutter

OBJECTIVES – A major processing difficulty arises in numerous coal conversion steps as a result of the tendency of common coals to soften and agglomerate when heated to process temperatures. One method of handling this problem uses oxidation at moderate temperatures to pretreat the coal to reduce its agglomerative tendency to an acceptable level. This research is studying the kinetics of this pretreatment experimentally to relate the data to proposed interpretive models and will correlate the kinetic data with the changes in coal properties. Seven coals from different sources are being tested at various temperatures and pressures, in fixed-bed reactors under a range of flow rates and for various particle sizes.

RECENT WORK AND ACCOMPLISHMENTS – Seven coals of varying rank (63 to 86 percent carbon), porosity (0.03 to 0.23 cm^3/gm), and moisture content (0.8 to 22.7 wt percent) have been dried and oxidized in two independent steps. Results show that significant amounts of CO_2 and CO are produced in the drying step, which is run in an inert nitrogen atmosphere at 150° to 300°C. Water removal appears to occur by a simple evaporation process, but carbonic gas evolution generally increases with coal porosity, moisture content, and temperature. Because of the carbon loss, the drying process can significantly reduce the energy value of the coal; furthermore, the subsequent oxidation rates are dependent on the conditions of drying. Rates of total oxygen consumption, oxygen fixation on the coal, and carbon dioxide, carbon monoxide, and water production have been measured. Results show that a large percentage of the oxygen consumed is fixed on the coal, up to 80 percent in some cases. Oxidation rate was found to increase with smaller particle sizes, but this effect is smaller for coals of large porosity, providing evidence for significant internal diffusive interactions with surface kinetics. A dilatometer test is being used to evaluate the changes that occur in the softening and expansion properties of the various coal samples. Results indicate that this new test is highly reproducible and vastly superior in this respect to the Foxwell gas flow test, over the range of particle sizes from 35 to 200 U.S. mesh and heating rates from 2° to 20°C/min. Additions to the coal of 10 wt percent inorganic salts reduced the swelling process up to 60 percent.

PLANS FOR THE COMING YEAR – Work will focus on completing the range of test variables and on selective drying and oxidation experiments to provide data for testing kinetic and diffusive models. An interpretation is also needed for the plastic changes that occur in bituminous coal to explain the observed effects of inorganic salt addition.

HYDROGEN DISTRIBUTION AND TRANSFER IN COAL HYDROGENATION SYSTEMS

UNIVERSITY OF PITTSBURGH
DOE - $110,431
9/20/77 - 8/31/79
Principal Investigator - S.H. Chiang

OBJECTIVES – This study of the behavior of hydrogen in coal hydrogenation systems is designed to achieve the following goals: to design, construct, and demonstrate a nickel-membrane hydrogen-probe for measuring hydrogen partial pressure and concentration in hydrogen/oil/coal and simpler system(s); to obtain equilibrium (steady-state) hydrogen distribution—in both elemental and chemically combined forms—in coal hydrogenation systems; and to study the dynamic (unsteady state or transient) behavior of hydrogen transfer between gas phase and condensed phase (liquid/solid mixture) in the system(s).

RECENT WORK AND ACCOMPLISHMENTS – Accomplishments have been made in equipment construction in that the design, acquisition, and construction of experimental facilities have been completed including a high-pressure test section and a low-pressure sampling section; hydrogen probe development in that a specially designed hydrogen probe has been successfully fabricated using a thin-membrane (0.003-in.-thick) nickel bellow with tests indicating that it is mechanically stable and has high hydrogen permeability; and hydrogen concentration measurement (in terms of partial pressure) in both gas and liquid phase in terms of the hydrogen permeation rate into or out from the nickel-membrane probe, with results agreeing well with theoretical relation that (Permeation Rate) = $K(P_1^{1/2} - P_2^{1/2})$, where K is the permeation constant and P_1 and P_2 are hydrogen partial pressures inside and outside of the hydrogen probe.

PLANS FOR THE COMING YEAR – The hydrogen probe will be used to conduct in situ measurements under simulated coal liquefaction conditions for hydrogen partial pressure and concentration in hydrogen/oil as well as hydrogen/oil/coal systems. The results will provide data for evaluating equilibrium hydrogen distribution and rate of hydrogen transfer in these multiphase systems.

HOT CORROSIVITY OF COAL GASIFICATION PRODUCTS ON GAS TURBINE ALLOYS

UNIVERSITY OF PITTSBURGH
DOE - $143,994; Pittsburgh U - $10,905
10/1/76 - 9/30/78
Principal Investigators - G.H. Meier, R.A. Stoehr

OBJECTIVES – This program seeks to develop information about the hot corrosion of gas turbine alloys in the environment likely to be found when a gas turbine is operated on low-Btu gas produced from coal in a fluidized-bed gasifier. It is designed to determine the mechanisms of attack and the major factors influencing the kinetics of hot corrosion in these environments. Existing gas turbine alloys and a few simple alloys of potential gas turbine alloy composition have been selected as representative of several different metallurgical types exhibiting different hot-corrosion behavior.

RECENT WORK AND ACCOMPLISHMENTS – The scope of the program includes: (1) gathering of data to ascertain the range of environmental conditions of importance in a turbine burning gasified coal; (2) thermochemical calculations to determine the important condensed-phase and vapor species to be expected in a turbine; (3) study of reactions between condensed-phase deposit mixtures and the oxides that form on turbine alloys; (4) simple high-temperature oxidation experiments on the alloys of interest; and (5) hot-corrosion experiments on the same alloys using the deposits that (1) and (2) indicate to be the most important. The results of (1) have indicated that Na_2S0_4, K_2S0_4, and their mixtures will be important species in condensed deposits and that contamination of these salts with $Si0_2$, $Ti0_2$, NaCl, KCl, C, $MgS0_4$, and $CaS0_4$ may be significant. In (2), the existing thermochemical data have been evaluated for pertinent metal-oxygen, metal-sulfur, metal-sulfur-oxygen, and metal-carbon-oxygen systems and both condensed phase stability diagrams and vapor species diagrams have been constructed at 1150°, 1250°, 1342°, and 1450°K for the metals Na, K, Mg, Ca, Al, Co, Cr, Mo, Ni, Si, Ti, V, and W. No new experiments have been conducted in (3). The alloys studied in (4) and (5) include commercial alloys such as IN-738, B-1900, FSX-414, and IN-657 as well as simpler laboratory alloys such as Ni-Cr, Ni-Cr-Al, Ni-Cr-Ti, Ni-Cr-Mo, Co-Cr, Co-Cr-Al, Co-Ti, and Co-Cr-Ti. The deposits are Na_2S0_4, K_2S0_4, CaS0 with and without additions of such contaminants as $Si0_2$, $Ti0_2$, C, and NaCl. The important conclusions are simple Cr_20_3-forming alloys of both Co and Ni have good hot-corrosion resistance to most of the deposits likely to form in turbines burning coal-conversion products with the exception of deposits containing considerable amounts of chloride; presence of carbide phases is detrimental to the hot-corrosion resistance of both Ni and Co alloys; complex alloy compositions characteristic of superalloys result in susceptibility to severe hot corrosion, the extent of which is sensitive to salt composition, particularly for Ni-base alloys; which suggests that uncoated alloys will not be able to provide the required combination of corrosion resistance and high-temperature strength for any of the components in turbines running on coal gas; and several alloys, including Co-18Cr-6Al-1Hf, Co-20Ni-27Cr, and Ni-50Cr, have corrosion resistance suitable for use as coatings and claddings.

PLANS FOR THE COMING YEAR — The study of the mechanism of hot corrosion of alloys using a wide range of salt deposits will be continued and intensified. Extensive electrochemical cell experiments are planned to elucidate the chemistry of the hot-corrosion reaction. Particular emphasis will now be placed on the hot corrosion of coating alloys such as Fe-Cr-Al, Ni-Cr-Al, and Co-Cr-Al. Finally, an extensive effort will be made to ascertain the separate and combined effects of chlorides in the salt deposits and $S0_3$ in the gas phase in the hot corrosion of superalloys and coatings.

SUPPORT TO CERAMIC TECHNOLOGY READINESS DEMONSTRATION

UNIVERSITY OF PITTSBURGH
DOE - $350,000
6/30/77 - 9/30/80
Principal Investigator - M.L. Williams

OBJECTIVES — The objective is to provide technical support to DOE in technology-readiness demonstration of electric-utility-size gas turbines operating at high inlet temperatures, using advanced state-of-the-art ceramic hot-section parts. The technical support will consist of direct support of program technical reviews, drawing on the extensive Department of Defense base of consultant expertise, data gathering and analysis, and special studies and technical tasks.

RECENT WORK AND ACCOMPLISHMENTS — All work performed has been in support of technical guidance for ongoing efforts devoted to design of advanced state-of-the-art, ceramic hot-section gas turbines and development of the Ceramic Gas Turbine Technology Readiness (CTRD) program plan.

PLANS FOR THE COMING YEAR — In early 1979, the CTRD program planning will be nearing completion; continuation of broad-base consultive support for this program is planned. Preliminary planning has been completed for execution of special technological support tasks in connection with experimental measurement of structural material corrosion/erosion performance in coal-derived combustion gas environments; experiments will begin in the forthcoming year..

HYDROGEN BONDING IN ASPHALTENES AND COAL

DUQUESNE UNIVERSITY
DOE - $162,000
4/1/78 - 3/31/80
Principal Investigator- N.C. Li

OBJECTIVES — This program will investigate the strength of hydrogen bonding and other molecular interactions that occur in asphaltenes and coal liquids, and to seek possible correlations of hydrogen-bonding strength with the viscosity.

RECENT WORK AND ACCOMPLISHMENTS — A direct calorimetric method has been used to determine simultaneously the molar enthalpy and equilibrium constant for quinoline (Qu) interaction with coal-derived asphaltenes (A), acid/neutral (AA) and base (BA) components of A, silylated asphaltenes (A(TMS)), and heavy oil (HO) fractions in benzene solvent. The linear variation of molar enthalpy values with the phenolic oxygen content of liquid fractions obtained from a given sample of coal has been attributed to the dominance of hydrogen-bonding effects, involving phenolic OH, over other types of molecular interactions in solution. In the Qu-A(TMS) system, the negative enthalpy values increase with a decrease in molecular weight of A(TMS), while the negative entropy changes increase with an increase in aromaticity of asphaltene fractions.

For the interaction between heavy oil and asphaltenes in benzene solvent, both viscosity and molar enthalpy change in the order BA > A > AA. These correlate well with the proton magnetic resonance downfield chemical shift of the OH signal of o-phenylphenol, as a function of added asphaltenes (A,AA,BA) concentration in CS_2 solvent. The results suggest that when asphaltene and heavy oil are present together, hydrogen bonding involving largely phenolic OH is one of the mechanisms by which asphaltene-heavy oil interactions are achieved and, in part, is responsible for the viscosity increase of coal liquids.

PLANS FOR THE COMING YEAR — To distinguish hydrogen bonding from other molecular interaction effects, ^{19}F-NMR measurements will be employed. Specifically, p-fluorophenol will be used as a hydrogen donor (O-H) to measure the shift of the ^{19}F signal as increasing amounts of a coal-derived liquid is added to a 0.01-m solution of the hydrogen donor in CS_2. This shift is a measure of the extent of all molecular interactions, including hydrogen bonding. Next, the shift of the ^{19}F signal of 0.01-m p-fluoroanisole as increasing amounts of the coal liquid are added to 0.01-m solution of p-fluoroanisole in CS_2 will be measured. The shift is now a measure of molecular interactions excluding hydrogen bonding because there is no hydroxyl hydrogen that can participate in hydrogen bonding. Comparison of the ^{19}F shift of p-fluorophenol and p-fluroanisole would give the chemical shift due to hydrogen bond formation. In addition, fluorobenzene will be used in place of p-fluorophenol to determine the amount of shift due to π-bonding interactions. Active investigation on characterization and study of interactions with coal liquids after various stages in hydroprocessing and upgrading will continue.

ANALYTICAL MODELING OF PRACTICAL COMBUSTION SYSTEMS

CLEMSON UNIVERSITY
DOE - $25,461; Clemson U - $1492
10/1/76 - 12/31/78
Principal Investigator - E. Bishop

OBJECTIVES — The objectives are to provide a validation test of one or more existing models of two-dimensional recirculating-flow combustion, to make an experimental evaluation of the various constants contained in these models, and to reach conclusions as to the most fruitful direction for further development work on such models.

RECENT WORK AND ACCOMPLISHMENTS — A comparison of the model with existing experimental measurements of combustion of propane premixed with air was carried out. The validation test included a parametric evaluation, using data comprised of various constants and empirical functions that appear in the model. The research focused on the ability of the model to predict the experimental trends that appear as the turbulence conditions are varied. Of interest was the ability of the model to describe the interplay between turbulence and chemical kinetics adequately.

PLANS FOR THE COMING YEAR — All work on this project will be finished shortly. The final report will be completed during April 1979.

CHEMICAL CONSTITUTION OF ALKYLATED AND DEPOLYMERIZED PRODUCTS FROM COALS

UNIVERSITY OF TENNESSEE
DOE - $100,000
4/1/77 - 9/1/79
Principal Investigator - J.W. Larsen

OBJECTIVES — The objective of this research project is to determine the molecular weight distribution of products from reductive alkylation and depolymerization of coals. Also, the product will be chemically and spectroscopically characterized.

RECENT WORK AND ACCOMPLISHMENTS — A pair of coals has been reductively ethylated and the molecular weight distribution of the products has been determined by a combination of gel permeation chromatography and vapor pressure osmometry. Of more significance are the results of control experiments performed using ^{14}C labeled naphthalene, THF, and ethyl iodide during the reductive alkylation. Virtually all of the naphthalene used reacts and forms a complex mixture of non-polar low-molecular-weight products. This mixture derives about half from naphthalene and about half from coal. Small amounts (about 4 to 6 percent by weight of the products) of THF are incorporated into the products. Some of this (~50 percent) is tightly adsorbed THF, which is not removed under vacuum at 90°, but will exchange with THF. Several coals have been depolymerized using Ouchi's modification of the Heredy-Neuworth technique. The coal-derived products (Bruceton coal) are principally high-molecular-weight materials ($>$ 80 percent above 2500). Much of the products are colloidal. In spite of this, average molecular weight (number average) in pyridine is 400 for the pyridine extractables from the depolymerized products. It seems likely that this reaction is limited by the accessibility of the reagents to the benzylic groups in the solid coal macromolecular network. It is possible that the low-temperature ($<$ 200°C) reactivity of coals may be controlled not by their inherent chemical reactivity, but by the accessibility of reagents to reactive groups in the interior of the coals.

PLANS FOR THE COMING YEAR – The molecular weight distribution of one more reductively alkylated and two more depolymerized products from coals will be determined. The rate of depolymerization (that is, the variation of molecular weight distribution of the products of a depolymerized reaction with time) is being measured. Experiments designed to probe the accessibility of the coal to reagents of various sizes will be performed.

EVALUATION OF COAL RESERVES IN WHITWELL SHALE

UNIVERSITY OF TENNESSEE
DOE - $22,378; Tennessee U - $ 8494
6/1/77 - 12/31/78
Principal Investigator: R. L. Wilson

OBJECTIVES – The intent of this work is to prepare the most accurate estimate possible on the coal reserves of the Whitwell Shale in Tennessee's Southern Cumberland Plateau based entirely on specific available data.

RECENT WORK AND ACCOMPLISHMENTS – Analytical data are being gathered on coals of the Whitwell Shale from published and unpublished sources. Markets, transportation, and active mines are also being studied. All data will be compiled by county. Coal thickness data points (sources include bore hole, outcrop, and mine workings) were gathered from the Tennessee Division of Geology files and from private sources. These data points were plotted on topographical base maps (scale 1:24,000). Mined out areas were also plotted. Coal reserve estimates were then made using methods based on rules adopted for this purpose by the U.S. Geological Survey (USGS) and the U.S. Bureau of Mines (BOM). These methods included subdivision of coal areas into measured, indicated, and inferred probability categories based on the data points and habit of the coal seam. Next, isopach maps were constructed within the arc areas, giving a good idea of the thickness distribution pattern of the coal, and making it possible to predict with more accuracy than would otherwise be possible trends in thickness away from the control points. The isopach lines subdivide the areas of measured, indicated, and inferred reserves into areas of less than 14, 14 to 27, 28 to 35, 36 to 41, and 42 in. or more. Average thicknesses were assigned to each of these areas, and strippable reserves separated from deep reserves by marking off coal beds with an overburden-to-coal ratio of 30:1 (ft) for strippable coal and thickness greater than 28 in. at depth for deep reserves. The final subdivisions were measured with a planimeter that gives a reading in square inches, which were converted into acres and the acres to tonnage by use of a formula that assumes that 1 acre ft of coal weighs 1800 tons. This formula is used by BOM and is based on actual mining experience. To arrive at a figure for recoverable reserves, further assumptions were made: for minimum thickness of coal, recoverable by underground mining, 28 in. and for average percentage of recovery, a conservative factor of 50 percent was used in all calculations; for minimum thickness for recoverable coal by stripping, 14 in. with an overburden-to-coal ratio of 30:1 (ft), and for recovery factor, 80 percent has proven to be accurate.

PLANS FOR THE COMING YEAR – This work is showing a 99 percent increase in recoverable tonnage when compared to a 1959 study by the Tennessee Division of Geology. The methods of determining the reserves are almost identical, but two major differences influencing the results are: acquisition of more data and introduction of modern strip mining technology. In the 1959 report, strippable reserves were not considered, wherein this estimate may show about a third of the reserves to be strippable. Coal less than 28-in. thick was not considered in 1959, whereas this work is including 14 in. and more (strippable - 30:1 overburden:coal). Total reserves to date are 364,210,000 tons, with the Sewanee Seam containing 299,490,000 tons.

COAL LIQUEFACTION AND DESULFURIZATION IN MULTIPHENOLS

UNIVERSITY OF HOUSTON
DOE - $40,000; Houston U - $1605
9/1/77 - 8/31/79
Principal Investigator - A. Attar

OBJECTIVES — The objectives are to obtain preliminary data on the feasibility of the use of multiphenols (Mp) for coal liquefaction and desulfurization. Mp were expected to permit liquefaction of coal at lower temperatures and pressures than conventional hydrogen donors.

RECENT WORK AND ACCOMPLISHMENTS — Four sets of experiments were conducted: liquefaction of Kentucky No. 9 in 1-methyl naphthalene solvents with or without Mp in the temperature range 170° to 400°C and pressures below 100 psi using the pyridine benzene and hexane solubles as a measure of the liquefaction; liquefaction of three coals in the temperature range 200° to 350°C and pressures below 100 psi using methanol, acetone, benezene, and pyridine solubles as a measure of the liquefaction; reference liquefaction tests with different Mp and/or different solvents; and tests on the kinetics of desulfurization using three different multiphenols. The most important results are that Mp enhance the rate of formation of benzene and hexane solubles from pyridine solubles; Mp help to produce desulfurized liquids with the sulfur evolving as H_2S or staying in the solid residue; Mp enhance the rate of liquefaction; the choice of solvent has a deterministic effect on the rate of coal liquefaction in Mp; and different-sulfur functional groups react with Mp at different rates.

PLANS FOR THE COMING YEAR — Liquefaction experiments using different solvents will be continued. The efficiency of using the donatable hydrogen in Mp will be determined, and the problems associated with separation of Mp from the liquefaction products will be considered. More detailed study of the effects of Mp on the sulfur content of the products will be performed.

HEAT SUPPLY TO FLUIDIZED BED BY PARTICULATE HEAT-TRANSFER MEDIUM

UNIVERSITY OF HOUSTON
DOE - $97,822; Houston U - $3485
8/77 - 8/79
Principal Investigator - R. Jackson

OBJECTIVES — The objective is to investigate heat transfer to a fluidized bed from larger or denser particles continuously passed downwards through the bed and removed from below. This method of heat supply can be used in endothermic reactions such as the steam gasification of coal. Concurrent feed of air or oxygen is then unnecessary.

RECENT WORK AND ACCOMPLISHMENTS – The first work phase, nearing completion, has been directed to identifying quantitatively those factors determining the holdup of descending particles in terms of their flow rate and finding the upper limits for the downflow of large particles. Holdup measurements have been made for limestone chips, various sizes of glass beads, and various sizes of lead shot descending through a 4-in.-diameter bed of polystyrene beads. Matching sizes of glass beads and lead shot have been used to assess independently the influence of particle size and particle density. The effects of bed depth and bed expansion on the rate of descent have also been explored. These studies have shown that residence times of the descending particles are usually quite long (of the order of a minute or more) so that they would be expected to come close to thermal equilibrium with the bed before leaving it. Thus, the maximum attainable heat-transfer rate is determined entirely by mechanical limits on the downflow rate. Measurements have confirmed that thermal equilibrium between the descending particles and the bed is closely approached. The "flooding point," which sets the maximum downflow rate, has been determined for each of the systems studied. Auxiliary studies in a two-dimensional fluidized bed have elucidated the mechanisms of particle descent and flooding.

PLANS FOR THE COMING YEAR – Measurements will be extended to beds of 6-in. diameter to assess the influence of bed diameter on holdup and flooding. The results will be summarized in correlations, including the influence of particle density, particle size, bed expansion, bed depth, and bed diameter on the holdup and flooding rates, which will be directly useful for the system design.

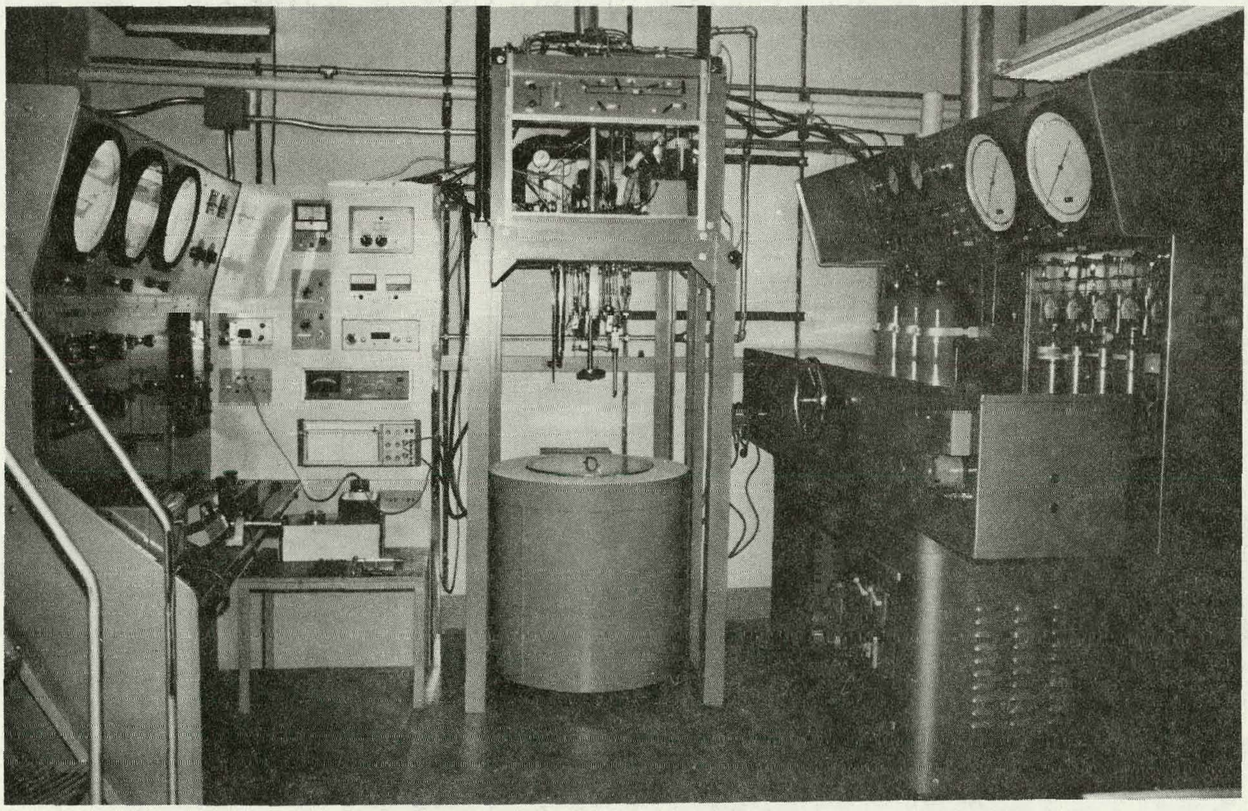
PHASE EQUILIBRIA IN COAL HYDROGENATION SYSTEMS

RICE UNIVERSITY
DOE - $247,973; Rice U - $15,000
4/1/76 - 3/31/79
Principal Investigator - R. Kobayashi

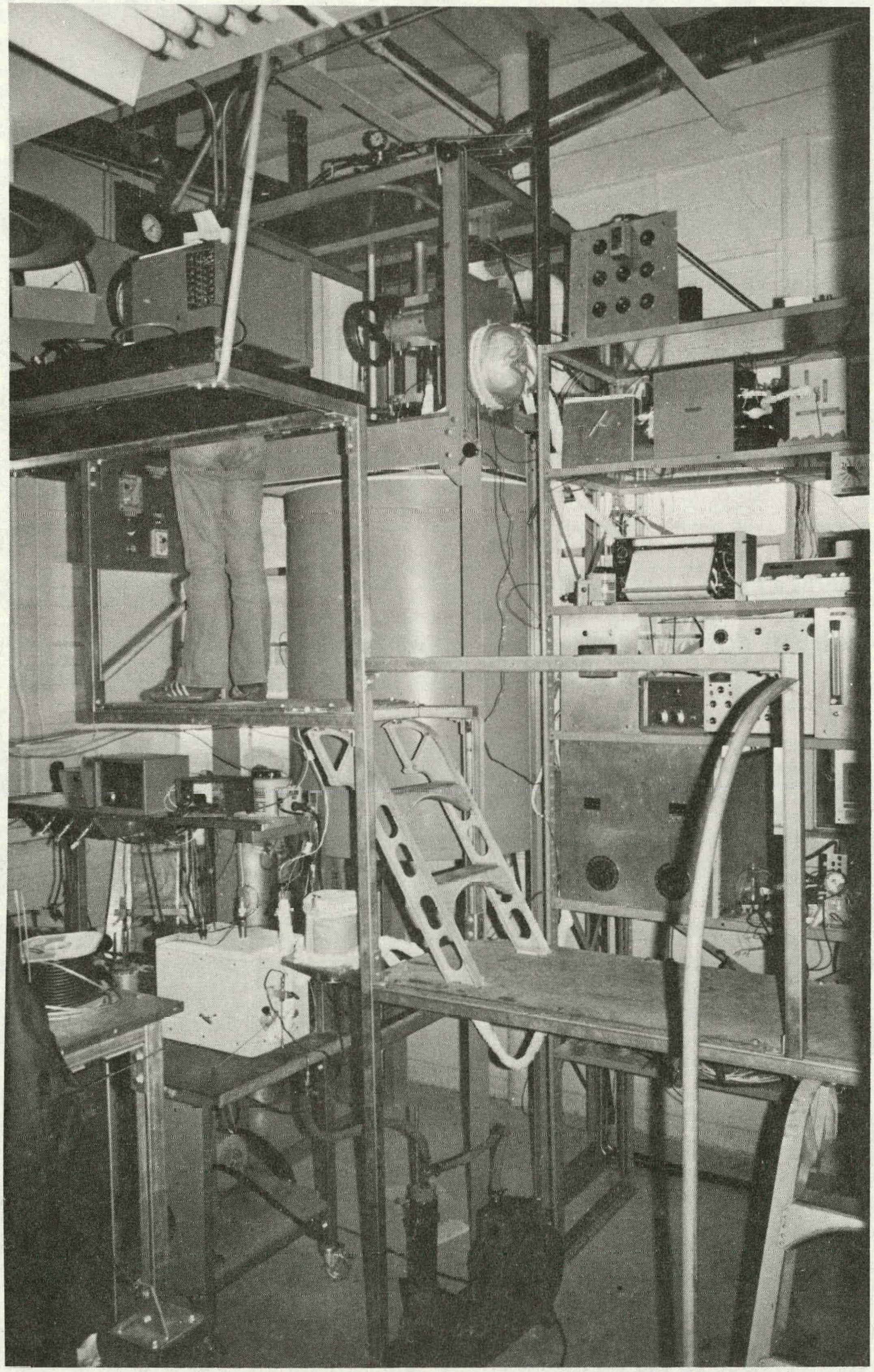
OBJECTIVES – The objectives are to design, construct, and exploit a high-temperature, high-pressure perturbation chromatography apparatus to obtain multicomponent vapor-liquid-equilibrium (V-L-E) and vapor-solid-equilibrium (V-S-E) phase data at both infinitesimal and finite concentrations; design, construct, and exploit high-temperature, high-pressure V-L-E and pressure-volume-temperature (P-V-T) measurements with high precision and convenience; and develop theories and software for the quantitative prediction of data obtained in the first two exercises.

RECENT WORK AND ACCOMPLISHMENTS – Both apparati are complete and being run to obtain preliminary data and to conduct the final debugging. Some of the unique features of the high-temperature, high-pressure perturbation chromatographic equipment are the incorporation of 1000-cc tandem pump for extremely precise flow and backpressure regulation; in-line ionization chamber capable of detecting perturbation of radioactive compounds (such as HT, $C^{14}H_4$, $C_2^{14}H_6$ with little or no distortions of the peaks; in-line thermal conductivity detector for the detection of infinite dilution perturbations; high-temperature, high-pressure chromatographic switching valves; high-temperature, high-pressure differential pressure indicator separating the fluids under study from the pressure measurement apparati; and other electronic apparati as needed to measure and/or control pressure, temperature, and perturbation chromatographic peaks. The V-L-E–P-V-T apparatus has tremendous versatility and ease of application. In fact, two such pump-equilibrium cells coupled together have been applied at milder conditions of temperature to measure both thermodynamic and transport properties—P-V-T, V-L-E, V-S-E, mutual and tracer diffusion coeficients and viscosities. The high-temperature cell pump, a beyond the state-of-the-art development, was pursued to confine the fluids under study within a single controlled-temperature environment. The V-L-E—P-V-T apparatus is being operated isothermally, but should also be applicable to conduct isochores (constants-volume or density) experiments. The outstanding features of the unit are the pump-cell in which the sample is confined; a magnetic pump in both which recirculates the vapor phase through the denser phases to hasten equilibrium; a diaphragm differential-pressure separator to isolate the ambient-temperature portion of the high-pressure system from the high-temperature portion; a high-temperature liquid bath equipped with heaters, stirrers, cooler, and so forth to enable precision control of the bath to within 10 millidegrees C; the superstructure necessary to raise and lower the bath and to exhaust the small amount of noxious fumes that are released from the bath; a sample preparation system including a gas volumetric pump and a liquid micro-volumetric pump; and other electronic apparati as needed to measure and/or control pressure, temperature, and chromatographic peak areas. Design and construction of the apparati were performed on the basis of incorporating the degree of sophistication developed at milder conditions at Rice University over the past 25 years into apparati operable under much more severe conditions of temperatures and pressures. It necessitated the development of many features considerably beyond the state of the art.

PLANS FOR THE COMING YEAR – The project will be completed and the final report submitted in March 1979.



Photograph of High-Pressure—High-Temperature Chromatographic Apparatus to Study V-L-E and Vapor-Solid Equilibria



Photograph of High-Pressure–High-Temperature Gas Solubility, V-L-E, P-V-T Apparatus

RHEOLOGICAL AND FLOW PROPERTIES OF METHACOAL SUSPENSIONS FROM TEXAS LIGNITE

TEXAS A&M UNIVERSITY
DOE - $35,778
9/1/77 - 6/30/79
Principal Investigator - R. Darby

OBJECTIVES – The rheological properties of suspensions of pulverized coal (lignite) in methyl alcohol (Methacoal) are being evaluated as a function of shear rate, solids concentration, particle-size distribution, and lignite moisture content. Representative measurements of the stability of these suspensions relative to comparable aqueous suspensions are also of interest. Construction of a small-scale tube flow facility to be used for obtaining pressure-drop versus flow-rate data for such suspensions is also included.

RECENT WORK AND ACCOMPLISHMENTS – Approximately 90 different samples of Methacoal suspensions have been produced representing variations in lignite moisture content, solids concentration, and particle-size distribution. Apparent viscosities have been measured as a function of shear rate in a specially designed concentric-cylinder viscometer, over about a 2-decade range in shear rate. The resulting data were fit by several simple pseudoplastic and plastic non-Newtonian models, and the model parameters were correlated with solids concentration and particle-size distribution. The viscosity was found to be an exponential function of solids volume fraction, which was essentially identical to the concentration dependence of viscosity for comparable aqueous suspensions. The influence of particle-size distribution upon viscosity could best be represented in terms of the relative amounts of particles above and below approximately 30 mμ in diameter. Suspension viscosities were found to exhibit a minimum as a function of this ratio, the specific value of which is dependent upon shear rate. This effect, and the degree of the viscosity reduction at the minimum, was more pronounced as the initial lignite moisture content was reduced. Measurements of sedimentation rates of comparable suspensions in both methanol and water media indicated that the suspensions reached an equilibrium concentration in methanol from one to two orders of magnitude faster in methanol than in water. Furthermore, the equilibrium suspensions in methanol were less compact and more fluid than those in water. A tube flow apparatus has been constructed for measuring pressure drop versus flow rate of these suspensions in laminar flow. Initial measurements on representative suspensions agree with the concentric-cylinder viscosity data, and extend these data to more than an order of magnitude higher in shear rate. A larger pipe flow apparatus is also under construction, which should enable obtaining a wider range of data including turbulent flow conditions. Additional work is being done to evaluate a continuous rotary homogenizer for use in producing larger quantities of suspensions, which will be required for operating the tube and pipe flow equipment. The conclusions drawn from the results are: the nature of the viscosity dependence upon solids volume fraction indicates that a Methacoal suspension that is 50 percent solids by weight would have a viscosity roughly one-third of that for a comparable 50 percent by weight aqueous suspension; suspension viscosity can be minimized by a judicial choice of particle-size distribution (i.e., fraction of solids smaller than 30 μ), depending upon the prevailing shear rate; Methacoal suspensions made from dry lignite exhibit superior properties (viscosity, stability) compared with those from more moist lignite; lignite solids settle faster and cleaner in methanol than in water and are less compact and more fluid in their equilibrium state.

PLANS FOR THE COMING YEAR – It is expected that construction and checkout of the tube flow facility will be completed by the end of June 1979.

NOVEL APPROACHES TO FUNDAMENTAL ORGANIC CHEMISTRY OF COAL STUDY

TEXAS A&M UNIVERSITY
DOE - $39,942; Texas A&MU - $3618
9/1/77 - 8/31/79
Principal Investigator - C.S. Giam

OBJECTIVES – The goal is to probe the basic structural and chemical features of Texas lignites and other coals using novel organic and organometallic reagents and reactions coupled with the modern separations-chemistry and analytical techniques. The liquefaction of coal and its conversion to fuel and organic feedstock require the development of efficient and environmentally acceptable processes whose design will depend upon an understanding of the fundamental organic chemistry of coal. Specifically, the proposed objectives are: the use of novel mixed sulfonic-carboxylic anhydrides to effect acylation of aromatic skeleta and hydroxyl groups as well as to depolymerize the coal structure under unusually mild conditions; and the application of a site-specific and highly selective lignin "unraveling" scheme involving thioacetic acid/boron trifluoride and Raney nickel to lignite degradation.

RECENT WORK AND ACCOMPLISHMENTS – The polymeric nature is mainly responsible for the insolubility of coal in organic solvents. Solubilization of the coal macromolecule by derivatization -depolymerization will assist the determination of the molecular structure of coal components. Once derivatized and depolymerized, the various fragments could be separated by such methods as high-pressure liquid chromatography, and liquid and gas chromatography. Fourier transform ^{13}C and ^{1}H nuclear magnetic resonance and coupled gas chromatography-mass spectrometry would then aid in the identification of degradation products. Derivatization and depolymerization reactions of Texas lignites were carried out using organochemical reagents. The lignite samples were demineralized by treatment with 2 N HCl, which decreased ash content from an original of about 20 to 5 percent. The lignite was then solvent extracted with benzene/methanol to remove the volatile components. After removal of solvents, samples were treated with octanoyl p-toluene sulfonate and acetyl p-toluene sulfonate, respectively. Based on benzene and toluene solubility, pyrolysis, and in some cases elemental analyses, there appeared to be small (approximately 10 percent) changes in the treated coal. Since the mixed anhydrides (generated in situ) are potentially powerful acylating agents, these conditions are not optimal. Alternative experimental conditions, such as longer reaction times, elevated temperatures, and high-pressure reactions, are being explored. The use of thiolacetic acid-BF_3 and mixed sulfonic anhydride reagents for derivatizing were expected to be especially useful in view of the high oxygen content of lignites. In this coal, at least part of the oxygen functionality could be represented by ether linkages. The preliminary results based on elemental and pyrolytic analyses appear to indicate a low degree of incorporation of substituents into the coal macromolecule. This incorporation, however had no significant effect on the solubility of the lignite in organic solvents. The thiolacetic acid-BF_3 degradation scheme, which was expected to involve breaking of ether linkages, was found to lead to the incorporation of about 1 S atom for every 45 C atoms. The program accomplishments are: refinement of a new technique for exposure of lignite samples to mixed carboxylic-sulfonic anhydrides; analysis of chemically treated lignites using the recently developed procedure for rapid and reproducible pyrolysis/gas chromatography of lignites; solubility studies to assess the extent of solubility enhancements via chemical treatment of lignites; the use of elemental analysis to assess the extent of chemical alteration of the coal polymer; refinement and adaptation of the Nimz lignin procedure to the degradation of lignite samples; comparative degradation of red oak by the Nimz procedure; analysis of the degradation products using infrared, proton, and carbon-13 nuclear magnetic resonance spectroscopy, and gas chromatography/mass spectrometry; and the discovery of a new and simple preparation of a tetramethylhexathioadamantane, a known antioxidant additive for lubricants.

PLANS FOR THE COMING YEAR — This work will be terminated on August 31, 1979.

ELECTROCHEMICAL ANALYSIS OF SURFACTANTS FOR ENHANCED OIL RECOVERY

TEXAS A&M UNIVERSITY
DOE - $48,403
9/78 - 8/80
Principal Investigator - C. Glover

OBJECTIVES — The objectives are: first, to characterize electrochemical reactions that can be used to analyze surfactants used in tertiary oil recovery, with initial studies concerned with aqueous systems but will be performed ultimately with the more pertinent oil-containing microemulsion systems; second, to apply these characteristics to the design or application of a continuous electrochemical detector for surfactant analyses. A successful detector will enable convenient measurement of surfactant concentrations and consequently lead to a large number of experiments that may be conducted in a reasonable length of time to evaluate difficulties with surfactant recovery processes such as surfactant adsorption or retention.

RECENT WORK AND ACCOMPLISHMENTS — Work to date has concentrated on project initiation and preliminary electrochemical investigations. Studies began with the platinum rotating-disk electrode. Problems with reproducibility and apparent adsorption of the surfactant onto the disk surface led to the use of a dropping mercury electrode. Studies are now being made on several sulfonic acid solutions and solutions of sodium dodecyl benzene sulfonate with terramethyl ammonium iodide as the supporting electrolyte.

PLANS FOR THE COMING YEAR — Studies related to the direct measurement of surfactants will be continued. Simultaneously, efforts will be made to apply indirect electrochemical methods to surfactant analysis. Inhibition of a known reaction by the surfactant or reaction of the surfactant to produce an electrochemically active specie that can be readily detected will be evaluated. It is anticipated that after 6 months a suitable method will have been selected and adapted to surfactant adsorption, at which time preliminary adsorption determination will begin.

FLUID TREATMENT FOR STIMULATION OF RESERVOIR SANDSTONES AND ENHANCED RECOVERY OF OIL AND GAS

TEXAS A&M UNIVERSITY
DOE - $50,000
9/1/78 - 8/31/80
Principal Investigator - W. H. Huang

OBJECTIVES — Specific objectives are twofold: to establish criteria and conditions that are technologically feasible for the matrix stimulation of sandstone reservoirs with alkali solutions at a minimum operating cost and to assess the applicability of the alkaline stimulation method to the field.

RECENT WORK AND ACCOMPLISHMENTS – Initial tests have been run on small plug samples, and improvement of permeability has been noted with certain solutions and conditions; for example, those of 0.2N NaOH at room temperature and those of 1.0N NaOH at 180°F. Greater or less concentrations of solution appear to affect permeability adversely, perhaps because of reaction products. Thus, a full-scale laboratory experiment is being undertaken to determine what rocks are most affected by sodium hydroxide treatment, the optimum conditions of pressure and temperature, and the optimum concentrations of solution and pore volume injection. Core samples, such as Berea sandstone, to be tested for the project have been characterized specifically on their matrix minerals—clay minerals and other physical and chemical properties of reservoir sandstones prior to alkaline leaching experiment. On the basis of experience in preliminary stimulation tests, effort has been made to modify the existing unit for laboratory stimulation tests so that results of the test will be more realistic and applicable to the field wells.

PLANS FOR THE COMING YEAR – Plans are that a new setup for a laboratory stimulation test will be completed; representative reservoir sandstones will be tested to determine the kinetics and mechanisms of matrix stimulation by alkaline solution; and characteristics of sandstones tested will be made to determine any significant changes in physical, chemical, and mineralogical properties of reservoir sandstones prior to and after the leaching experiment.

FACULTY/STUDENT PROGRAMS AT BETC, GFETC, AND LETC

ASSOCIATED WESTERN UNIVERSITIES, INC.
DOE - $315,500
6/76 - Continuing
Principal Investigator - D.I. Walker

OBJECTIVES – This program will provide education and training opportunities for faculty and students from primarily Western universities to become acquainted with and directly involved in fossil fuel research problems faced by the three Western Energy Technology Centers (ETC) and to permit qualified faculty members to assist Technology Center staffs in finding solutions to fossil energy problems being explored by the Centers.

RECENT WORK AND ACCOMPLISHMENTS – The program originally began in 1976 during the summer months at the Laramie Energy Technology Center. During the summer of 1978, the programs expanded to all three Western Energy Technology Centers. From September 1978 to January 1979, six graduate students were assigned to perform research for the GFETC, which will result in completion of requirements for their higher degrees. Areas involved in the research assignments include in situ coal gasification, oil shale retorting and subsequent environmental controls and analyses of off-gasses and liquids, computer programming, tar sand extraction methods, and chemical thermodynamics of fuels. Summaries of both technical and administrative aspects of each assigned project were prepared by the participants and provided to Center Directors and to the DOE Office of Field Coordination and Institutional Affairs.

PLANS FOR THE COMING YEAR – The program will continue at the three Centers in the same manner as before, with the exception that more graduate students will be supported while they are performing research on their own campuses. Thus far, this program has been implemented only for the GFETC, but it could be expanded to include the other two Centers if requested. The program for this year will also include several part-time appointments during the year for faculty members, as well as the full-time summer appointments. The FY 1979 funding is anticipated at \$48,500 for LETC and GFETC and \$48,000 for BETC.

ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

BRIGHAM YOUNG UNIVERSITY
DOE - \$156,738; Brigham Young U - \$9474
9/20/77 - 9/19/79
Principal Investigator - C.H. Bartholomew

OBJECTIVES — This research program will assist DOE and its contractors in evaluation of new catalyst technology for upgrading coal-derived gases to synthetic natural gas. One of the most serious problems with presently available catalysts is sulfur poisoning at very low H_2S concentrations. Accordingly, development of more sulfur-tolerant catalysts would constitute a major technological advance in the methanation process. Other potential breakthroughs such as development of catalysts that operate at higher temperatures, higher-space velocities, and low H_2/CO ratios need to be explored. Research focused on development of new bimetallic catalysts which are more efficient and stable than commercially available methanation catalysts and evaluation of new monolithic ceramic catalysts which may have important economic and technical advantages in the methanation process because of their higher activity and lower pressure drop at high-space velocities relative to pellets. The research objectives include careful characterization of each catalyst, a study of methanation kinetics at high pressures, and investigation of catalyst deactivation by sintering, sulfur poisoning, and carbon deposition. Close communication with other researchers and interaction with other contractors to promote large-scale testing and development of the best catalysts is an important aspect of the program.

RECENT WORK AND ACCOMPLISHMENTS — During the past year, significant accomplishments were made: sulfur poisoning studies of nickel, cobalt, and nickel bimetallic catalysts; a comparative study of the methanation activities of monolithic and pellet-supported catalysts over a wide range of reaction conditions; and an investigation of the thermal stability and resistance to carbon deposition of nickel and nickel bimetallics during high-temperature methanation. In activity tests of alumina-supported Ni, Co, and Ni-Co catalysts before and after exposure to 10 ppm H_2 in 450°C, a greater specific activity was observed for fresh and poisoned samples of Ni-Co; or, in other words, a synergistic (possibly alloying) effect relative to Ni and Co. Effects of exposure to 10 ppm H_2S during reaction on methanation activity of similar Ni, Co, and Ni bimetallic catalysts in powder, pellet, and monolith form were also investigated. Results of these experiments at 250°C, 1 atm, and a space velocity of 30,000 h^{-1} with 10 ppm H_2S in the reactant stream show that cobalt and most nickel bimetallic catalysts are not significantly more or less sulfur tolerant than nickel; Ni-MoO_3, however, is more active before, during, and after exposure to H_2S. The data also indicate that monolithic catalysts are significantly more sulfur tolerant than either powder or pellet catalysts. All of these catalysts, however, are almost completely deactivated within a period of 2 to 3 days under the conditions investigated.

The catalytic activity and selectivity of pellet and monolithic supported Ni/Al_2O_3 for methanation of carbon monoxide were investigated to determine the role of support geometry in catalysts performance. Turnover numbers, CO conversion versus temperature data, and product distributions were measured at space velocities from 15,000 to 50,000 hr^{-1} and pressures of 1.4 to 25 atm. The data show that monolithic-supported nickel is significantly more active and selective for methane production at both low and high CO conversion compared to nickel catalyst beads and pellets. Monolithic-supported methanation catalysts apparently operate with a higher effectiveness factor and rate of mass transfer than do catalyst beads or pellets. Because of its superior activity, selectivity and low-pressure drop at high-space velocities, monolithic nickel may be the ideal catalyst for use in a high-throughput recycle methanator.

During the past 4 years, several unique nickel and nickel bimetallic catalysts have been developed in this laboratory for methanation of coal-derived gases. To compare the performance of these new catalysts with commercial methanation catalysts under realistic industrial conditions, a series of high-temperature, high-pressure tests were carried out during the past 6 months. These tests involved the measurement of methanation rates in a fixed bed or recycle reactor at 25 atm as the temperature was increased slowly (2°C/min.) from 200° to 550°C using a reactant gas containing 64 percent CH_4, 16 percent Ar, 14 percent H_2, 4 percent CO, and 2 percent CO_2. CO conversion versus temperature data show that catalysts prepared in this laboratory are more active than commercial catalysts. Hydrogen chemisorption measurements and chemical analysis of samples before and after reactor tests establish that carbon deposition and sintering are responsible for the loss of activity at high temperatures.

Technical communication and visits to other methanation laboratories are vital aspects of the research program. The Brigham Young University laboratory is presently active in communication with more than 12 other laboratories in the United States and Europe. Training of students is another important part of this program.

PLANS FOR THE COMING YEAR – Investigation of monolithic-nickel catalysts with different geometries is continuing. Construction of two new recycle reactor systems (one quartz and one stainless) has just been completed. The quartz reactor will be used in the coming months to investigate methanation kinetics of nickel, ruthenium, and nickel bimetallic catalysts in the absence and presence of dilute H_2S at low pressures. The stainless steel Berty reactor will be used to study methanation kinetics at high pressure (up to 75 atm). Physical and chemical properties of each catalyst will be characterized by means of chemisorption, Auger, ESCA, X-ray, and electron microscopy measurements. Closer interaction with industrial and government researchers to achieve large-scale testing of the best catalysts is also planned.

MIXING AND GASIFICATION OF COAL IN ENTRAINED FLOW SYSTEMS

BRIGHAM YOUNG UNIVERSITY
DOE - $244,378; Brigham Young U - $12,862
5/1/77 - 4/30/79
Principal Investigators - L.D. Smoot, P.O. Hedman

OBJECTIVES – This program will identify physical- and chemical-rate processes that control gasification of pulverized coal. A series of basic experiments are planned where gas-particle samples are obtained from inside a laboratory gasifier and analyzed to determine rates of gas mixing, coal-particle dispersion, and coal reaction together with temperature and gas and solids composition. Related cold-flow experiments with probes are being conducted to determine rates of gas and particle mixing in the absence of chemical reaction. One- and two-dimensional computer codes are being developed to describe the details of entrained coal gasification processes.

RECENT WORK AND ACCOMPLISHMENTS – Installation of the entire laboratory gasification system was completed, including the high-pressure control system, improved coal feeder, cyclone-particle separator, probes, sample train, and instrumentation. Sixty-three trial gasification tests were conducted at atmospheric pressure to demonstrate flame stability in coal-oxygen-steam systems (11 tests), to evaluate and improve probes and sample train system (40 tests), to check feed and control systems (7 tests), and to obtain preliminary test data (5 tests). All tests were performed with a HV bituminous coal of about 50 μm mass mean coal-particle diameter. Characterization of the test coal was completed, as were 85 cold-flow mixing tests. Eighteen of these cold-flow tests were performed to check out the laboratory gasifier. The balance was conducted in a separate cold-flow facility and assymmetry effects were resolved. Test variables included particle size (24 μm, 46 to 48 μm), particle type (silicon, coal dust), test chamber diameter (two levels), and test chamber length. Test results suggest that the coal dust particles dispersed more rapidly than the silicon, small particles disperse more rapidly than larger ones; the secondary air injection angle significantly enhances mixing, and neither chamber diameter or length greatly influence gas rates of particle mixing. Design of a new inlet system to introduce swirling flows into the mixing chamber was completed. Development of a one-dimensional computer code for entrained coal gasification processes was completed, and detailed documentation of the code was initiated. Code efficiency was improved, and analytical stiffness problems were resolved. A series of computations suggested that particle heatup and char oxidation rates were particularly important rate-controlling processes. Effects of particle-size distribution were demonstrated. Computations compared well with laboratory combustor data, and additional computations were made for three different entrained gasifiers being developed by industry.

Development of a generalized two-dimensional gasification code was completed for gaseous systems. Statistical treatment was incorporated to account for the observed irregular nature of such fluctuating, reacting media. A series of computations demonstrated the importance of initial turbulence levels and of careful specification of numerical grid sizes. Results from additional computations compared well with laboratory combustor data for a natural gas-air system, and predictions were also compared with cold-flow measurements. Preparation of a book was completed which provides a detailed basis for modeling of pulverized coal gasification.

PLANS FOR THE COMING YEAR – A series of gasification tests will be performed to determine the range of coal-oxygen-steam compositions that can be stabilized in the laboratory gasifier and to provide the first detailed test results on rates of gasification processes. The first cold-flow tests with swirl will be conducted as well as cold-flow tests at high pressure. Documentation of the one-dimensional coal gasification code will be completed, and work will be initiated to extend the two-dimensional code to gasification of pulverized coal.

SIALON REFRACTORIES FROM CLAY AND COAL

UNIVERSITY OF UTAH
DOE - \$222,197; Utah U - \$5464
6/1/76 - 5/31/79
Principal Investigator - I.B. Cutler

OBJECTIVES — Sialon, a solid solution of silicon nitride and aluminum oxynitride, can be obtained by reaction from clay and coal with nitrogen. Sialon is similar to silicon nitride; but unlike silicon nitride, sialon can be sintered to near theoretical density much like alumina. A practical scheme for producing kilogram quantities of sialon in the form of powder and refractory brick has been devised and tested in the laboratory. The high-temperature properties of sialon are sensitive to impurities. Some impurities are detrimental to the hot strength of sialon and some aid in the sintering of sialon. These initial results will be explored further, and optimization of high-temperature properties will be the objective of continued research. This new material will approach and perhaps surpass hot-pressed silicon nitride in strength at high temperatures. Some impurities that accompany the ash in coal and clay are incorporated into the sialon solid solution. Other impurities, such as calcium and iron, end up in second-phase material and contribute to low hot strength of sialon. This research will explore more fully both types of impurities and minimize the second-phase impurities selecting the type of clay and coal used and by simple processing steps that will eliminate offensive impurities. Fabrication and testing of high-strength sialon will be a further goal.

RECENT WORK AND ACCOMPLISHMENTS — Extruded clay-coal pellets have been reacted in nitrogen 1400°C to produce sialon with a single phase β' silicon nitride structure. A simple laboratory apparatus has been developed to produce sialon powder at a rate of approximately 1 kg/d. Although not all reaction parameters have been optimized, a dozen refractory bricks with just over 20 percent porosity have been fabricated. Sialon from the clay-coal-nitrogen reaction yields a powder that is more suitable for sintering than any previously reported. Sintering of sialon powder to about 95 percent of theoretical density has been achieved at 1650°C compared with 1750°C reported in other laboratory tests. Alumina is one of the impurities often found in sintered sialon. Mullite and alumina are intermediates in the reduction and nitridization of clay. Alumina may be retained as a second phase if insufficiant carbon is mixed with clay. Various amounts of alumina can be sintered with sialon, and compositions varying in thermal expansion coefficient from about $2.6 \times 10^{-6}/^{\circ}C$ to more than $8 \times 10^{-6}/^{\circ}C$ can be readily fabricated. Sialon containing residual alumina may be sintered with magnesia to produce a sintered sialon with sialon and spinel in solid solution with the beta silicon nitride structure. Considerable amounts of spinel can be incorporated into this structure. Iron as an impurity can be found in sintered sialon as melted globules of ferrosilicon and catalyzes the sialon formation at 1400°C but does not add to the desirable properties of sintered sialon. The hot strength of sintered sialon made from clay and coal was measured by a flexure test. The impurities in the clay and coal are responsible for the creep-type failure that occurs at high temperatures.

PLANS FOR THE COMING YEAR — Of primary concern for the elimination of impurities will be selectivity in the clay and coal used to obtain sinterable sialon powder. Inasmuch as calcium appears to form stable silicates in silicon nitride fabrication, it is suspect in sialon formation. Low calcium containing clays and coals will be explored. For removing iron, methods of solution will be investigated following formation of sinterable powder. Magnetic separation techniques are not as applicable as acid solution. Fabrication techniques will be used to obtain high-strength sintered sialon, by eliminating impurities and defects from porosity and unwanted inclusions.

PROCESSES FOR LIQUEFACTION AND GASIFICATION OF WESTERN COALS

UNIVERSITY OF UTAH
DOE - $2,930,966; Utah U - $264,120
6/1/75 - 5/31/79
Principal Investigator - W.H. Wiser

OBJECTIVES — The 16 different research projects conducted in connection with this contract cover evaluation of process concepts for liquefaction and gasification of coal; studies of the fundamentals of catalysis as applied to coal liquefaction and gasification; studies of the mechanisms involved in coal liquefaction and gasification; and determination of the properties of coal and coal conversion products. The information developed in these studies will assist in optimization of coal liquefaction and gasification processes, will assist materially in the application of coal to the solution of energy problems now facing the United States and other nations, and will provide parts of the basic training for students, particularly at the graduate level, who will eventually assume responsible positions in the industries associated with energy production, conversion, and utilization.

RECENT WORK AND ACCOMPLISHMENTS — A simple process is needed to upgrade coal into a liquid that is compatible with petroleum. Pursuant to this need, a study was conducted at the University of Utah to determine the range of possibilities with free radical or vapor-phase catalytic reactions between coal and hydrogen. The first step in the study involved determining the effects of hydrogen on pure compounds such as aromatics, naphthenes, and paraffins at high temperatures and short residence times. A wide variety of heavy hydrocarbons including heavy coal liquids, tar sand bitumens, heavy native oils (Cold Lake), and petroleum residues were upgraded to lighter oils resembling crude oils in flow properties and chemical composition. Studies are being performed to determine the feasibility of converting coal to liquids by much simpler means than now available. The studies on pure compounds have elucidated the mechanism of many of the important reactions taking place between hydrogen and hydrocarbons. A new process has been determined which upgrades a wide variety of heavy hydrocarbons, including coal, to much lighter liquids. This noncatalytic process has high-reactor efficiency at moderate temperatures (400^{o} to $600^{o}C$) and pressures (250 to 2000 psi) and involves low hydrogen input (1 to 2 percent). In recent studies, catalysts have been developed that give improved selectivity of C_2 to C_4 hydrocarbons from CO and H_2. Studies of coimpregnated copper-cobalt-alumina catalysts have demonstrated an enhanced selectivity for C_2 to C_4 production, the optimum occurring at a Cu/Co ratio of about two. Catalyst characterization studies revealed a synergism in this catalyst system in which the Cu helped reduce the CO, and the Co aided in dispersing the Cu phase. An alloy or bimetallic cluster is responsible for the change in catalyst selectivity. Although C_2-C_4 selectivities as high as 50 percent were achieved, the olefin-to-paraffin ratios were less than unity. Studies on precipitated, promoted iron-based catalysts have also been encouraging. A manganese-iron catalyst formulation having high activity gave 55 percent C_2-C_4 products with an olefin-to-paraffin ratio of four. Work is continuing on a number of different promoter formulations for iron and other promising catalysts to allow selection of optimum catalysts.

Using carbon-13 NMR (CMR) spectroscopy as a tool, whole coal liquids have been examined as well as the liquid and gaseous fractions thereof. The ability of CMR spectroscopy to explain structural differences has been used in establishing chemical structural units present in the liquids. CMR spectra on solid coal have been obtained and compared with the spectra obtained on the liquids produced from the solid coal. In high-volatile bituminous coal from Clear Creek, Utah, the liquid spectra closely resemble those observed for the solid. One major spectral change is observed in the comparison, occurring at a few carbon centers of a relatively well defined structural type. The general similarity of the liquid and solid spectra is currently being studied. A computerized equilibrium thermodynamic correlation for the coal-hydrogen-steam system (no molecular oxygen) has been prepared, indicating achievable heating values for ratios of steam to H_2 in the feed.

PLANS FOR THE COMING YEAR — This project will be terminated May 31, 1979. Until that time, effort on the various projects will continue to obtain further understanding of the principles, mechanisms, reaction parameters, and products involved.

STABILIZATION OF ROTATING MACHINERY FOR FOSSIL FUEL

UNIVERSITY OF VIRGINIA
DOE - $319,667; University of Virginia - $41,375
8/15/76 - 8/14/79
Principal Investigator - D.W. Lewis

OBJECTIVES — This research provides information on the dynamics of rotating machinery in a format suitable for use by both industries that manufacture and those that use rotating equipment. This work will provide design guides and criteria to evaluate machine performance from the dynamics and stability viewpoint and provide diagnostic information which can be used for preventative maintenance by equipment users. Computer programs that analyze machine dynamics and stability by mathematical simulation, together with manuals describing their theory and use, will be made available to industry.

RECENT WORK AND ACCOMPLISHMENTS — Experimental work with preloaded four-lobe bearings showed the importance of orientation regarding the speed of the instability threshold. With a 3000 rpm critical speed, oil whip occurred between 6600 and 12,500 rpm, depending upon bearing orientation. There was good theoretical correlation with experimental work regarding the onset of instability of a three mass rotor with step bearings. This complements the extensive theoretical work showing the optimum depth of the step for this type bearing. An analytical correction factor to account for the two-dimensional effects has been derived for plain cylindrical journal bearings. This is a short-cut for determining the nonlinear dynamic forces and motion of a journal.

PLANS FOR THE COMING YEAR — The ranking of the effectiveness of different types of fixed pad bearings against instability driving mechanisms for different shaft flexibilities and speeds will be completed. The results of this program will be presented.

GAS-SOLIDS INTERACTIONS IN FLUIDIZED-BED DISTRIBUTION ZONE

UNIVERSITY OF VIRGINIA
DOE - $116,947; University of Virginia - $3055
6/15/76 - 10/31/78
Principal Investigator - D.J. Kirwan

OBJECTIVES — This program will investigate the interactions between gases and solids in the distribution zone of a fluidized bed with particular emphasis on delineation of the regimes of stagnant (defluidized), moving but nonfluidized, and fluidized solids. Improper design of the distribution system for gases entering a fluidized bed can have a number of deleterious effects. Successful correlation of solids distribution patterns with distributor geometry and operating variables such as bed superficial velocity, gas entry velocity, and entry port spacings will lead to improved distributor design methods for large-scale fluidized-bed installations involving coal.

RECENT WORK AND ACCOMPLISHMENTS – The use of a miniature self-heating thermistor probe to identify the type of gas-solids behavior in the distribution zone of a fluidized bed was extended to the detailed probing at ambient temperature of two reactors, each within seven 0.5-in.-diameter air entry ports on a triangular pitch and containing 60μ petroleum cracking catalyst. The 19-in.-diameter unit was tested at an entrance velocity of 200 ft/sec and a superficial velocity of 1.0 ft/sec; the 13-in.-diameter unit was tested at the same entrance velocity and a superficial velocity of 2.0 ft/sec. Both reactors were probed with air entering at the probing plate and with air entering upflow 2 in. above the probing plate. The results of these probings were used to develop three-dimensional plots of the several gas-solids regimes under the conditions of test. No nonmoving solids were detected in the area between the center and the peripheral air entry ports for either the 13-in. or 19-in.-diameter unit.

PLANS FOR THE COMING YEAR – Experimental work on the contract has been completed.

STIRRED-TANK REACTOR EXTRACTIVE COAL HYDROGENATION PROCESS

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
DOE - $191,996
6/27/74 - 10/1/78
Principal Investigator - G.H. Beyer

OBJECTIVES – This research intends to economically convert coal to a clean solid and/or liquid fuel by developing and applying chemical engineering techniques to improve process flowsheets by using a continuous stirred-tank reactor with residence times long enough to degrade the coal for sulfur removal, yet short enough to minimize hydrogen consumption.

RECENT WORK AND ACCOMPLISHMENTS – Experiments with tubing bombs have shown that industrially important coals can be made soluble in pyridene by heating to 400°C for only 2 to 5 minutes. A loop reactor, which acts as a continuous stirred-tank reactor, accomplishes rapid heating with excellent heat and mass transfer. Loop residence times of 7 min. at 425°C have produced "prompt coal", a highly reactive coal containing the early decomposition products on a continuous basis. Substantial amounts of sulfur have been removed using only the hydrogen in the coal itself. The solvent used to slurry the coal has been a nondonor mineral oil which is stable at reactor conditions. Experience with the loop reactor suggests that the long residence times characteristic of SRC process flowsheets may be materially shortened by using a plug-flow reactor to provide 2 to 5 min. of residence time to make the coal pyridene-soluble, followed by a loop reactor to stabilize the reactive products. Using this approach, coal may be modified avoiding slow dissolution and laborious separation steps.

PLANS FOR THE COMING YEAR – Funding for the project terminated.

CO DISINTEGRATION OF REFRACTORIES IN COAL GASIFIERS

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
DOE - $132,559; VPI and SU - $8476
6/1/77 - 5/31/79
Principal Investigator - J.J. Brown

OBJECTIVES — This investigation seeks to determine whether or not CO disintegration is likely to occur in the refractories used in coal gasifiers and to define the conditions under which this can be expected to become a serious problem.

RECENT WORK AND ACCOMPLISHMENTS — Various aspects of CO disintegration of three refractory compositions have been examined: 90+ weight percent Al_2O_3, 50+ weight percent Al_2O_3 calcium aluminate bonded castables, and 90+ weight percent Al_2O_3 phosphate bonded ramming mix. Each composition was doped with 0, 0.5, 1.0, 1.5, and 2.0 weight percent (iron equivalent) Fe and Fe_2O_3. The compositions were prepared as 2-in. x 2-in. cubes according to conventional procedures, and four samples of each composition were exposed for 100 hr at 500°C to the various gases at a gas flow rate of 5 ℓ/hr. More than 1000 samples were examined according to ASTM specifications and their compression strengths measured.

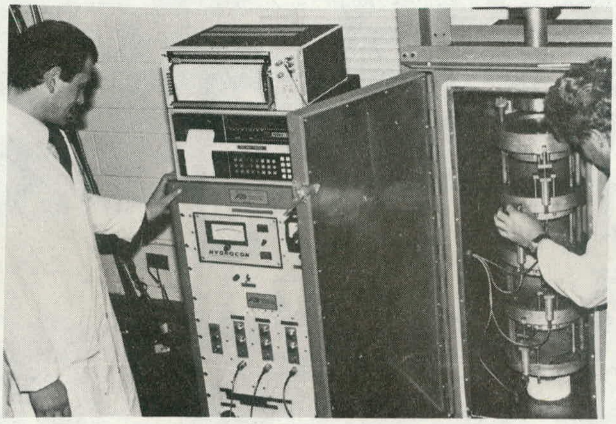
According to the results of this investigation, high alumina castable and phosphate bonded refractories will degrade fairly rapidly through CO disintegration. High pressure greatly accelerates this behavior. It has not been determined what combinations of pressure and temperature are most damaging; nor is it known if gaseous additives that have retarding and/or accelerating effects at atmospheric pressure behave in a similar manner at 500 or 100 psi pressure. Based on recent results, some high alumina castables not doped with any iron additive will show serious disintegration after several hundred hours at about 500 psi in a CO-containing environment. Iron levels of 0.5 weight percent or less are sufficient to cause serious refractory disintegration at 500 psi. The particle size and chemical form of the iron impurity was found to be important to the mode and rate of CO disintegration. In addition, H_2O, NH_3, and H_2S were found to be the most important gaseous additives to CO.

PLANS FOR THE COMING YEAR — This program will continue to design and evaluate the performance of the three refractory compositions under actual coal gasification operating conditions. Present experiments at 500 psi/500°C/100 hr (low iron levels) will be expanded by introducing steam, NH_3, and H_2S gaseous additives. Experiments at 1000 psi/500°C in CO with those additives that showed the most drastic effects at 500 psi will be conducted and repeated at a reduced temperature. The effect of particle size of iron impurities under the most severe disintegration conditions will be investigated, as well as the possibility of reducing the catalyzing effect of the iron impurity by glass or compound formation through pre-exposure washes or heat treatments.

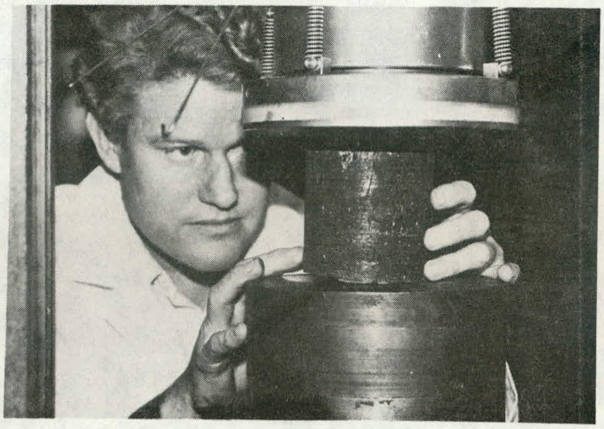
DESIGN OPTIMIZATION IN UNDERGROUND COAL SYSTEMS

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
DOE - $456,000; VPI and SU - $81,000
12/10/73 - 6/6/79
Principal Investigators - J.R. Lucas, C. Haycocks

OBJECTIVES — This research intends to stress those activities that would maximize coal extraction and increase the coal production capability of many U. S. underground mines. It will be necessary

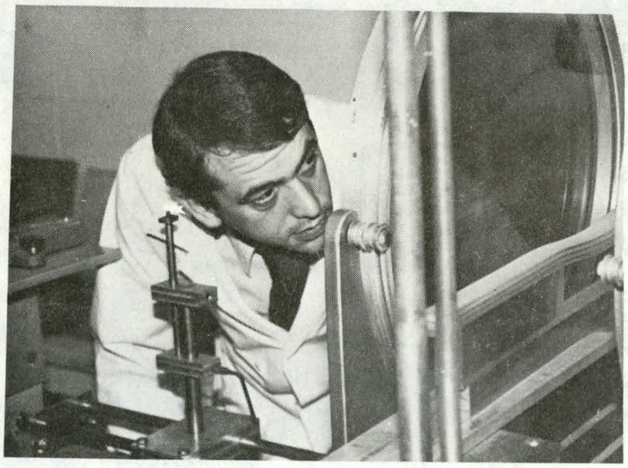


Researchers Prepare a Creep Machine for Testing Before Preforming an Experiment

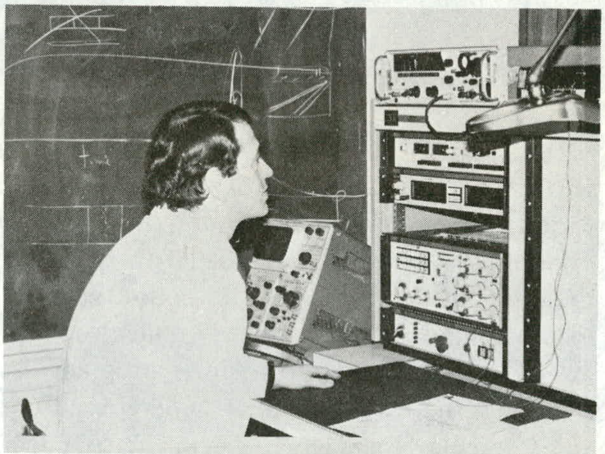


Researcher Adjusts a Coal Specimen Prior to Testing

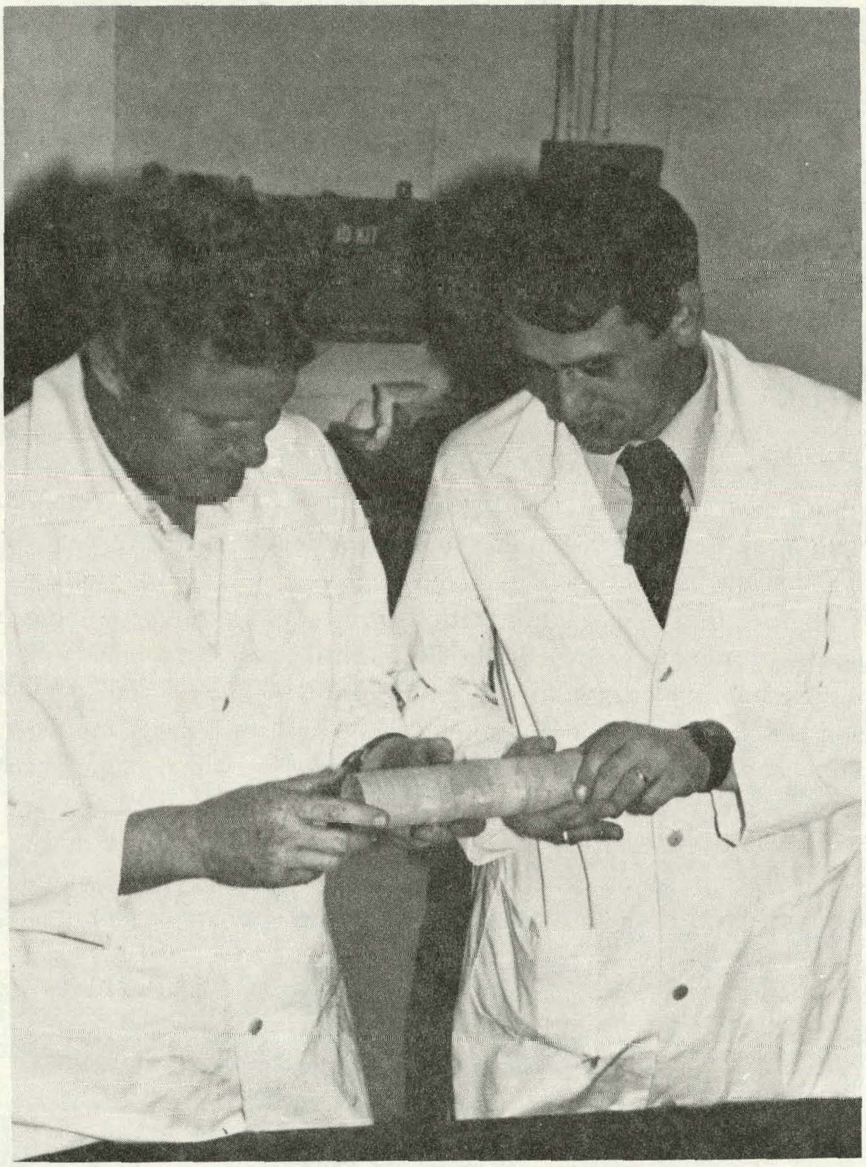
to develop a relationship between the cubical and cylindrical strengths of coal to facilitate use of exploration drill core data for design of underground coal mines. This study will facilitate mine planning and evaluate ultimate extraction ratios from exploration diamond-drill data prior to actually engaging in the mining process itself. This will increase subsequent mining efficiency by contributing to the establishment of firm planning prior to mining activity. A longwall mining simulator is being developed using both borehole and underground sampling data to facilitate equipment selection and planning of longwall operations. The primary aim of the simulator is to increase the efficiency and avoid some of the past failures in longwall mining. A primary objective of the research is to increase the efficiency and application of the support system in underground coal mining by using the roof-truss principle. A variety of systems and economic analyses will be performed on various aspects of underground coal mining to improve production and minimize cost while increasing efficiency.



Researcher Uses a Polariscope for an Experiment Concerning Roof Control

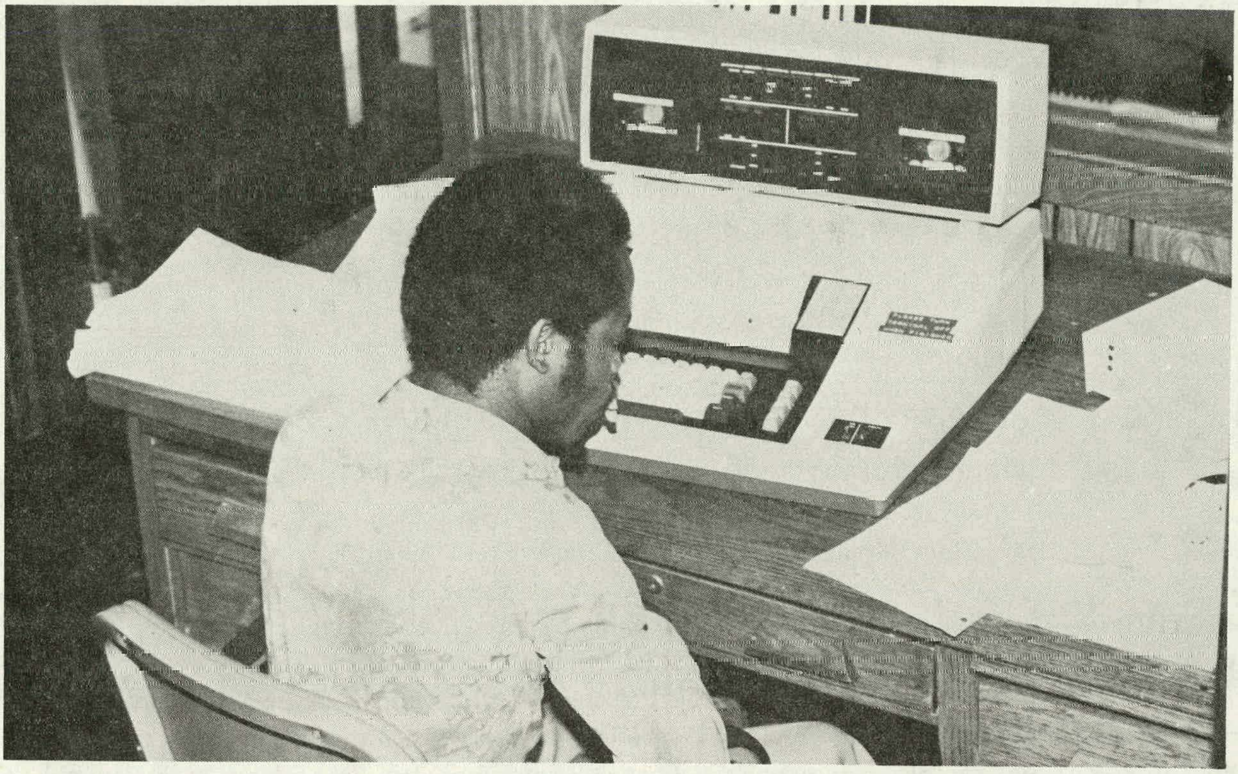


Researcher Adjusts the 1-MM lb, Stiff-Testing Machine for a Test on Coal



Researchers Examine a Specimen of a Core from a Coal Mine Roof

RECENT WORK AND ACCOMPLISHMENTS – A longwall simulator, capable of representing various strata conditions around a proposed longwall face, including heading widths and pillar dimensions in both head- and tail-entry panels, has been completed, as well as an economic study determining the optimum economic length of a longwall face. A versatile simulator for the use of load-haul-dump (LHD) units in underground coal mines was developed. Work aimed at combining available simulators into a single program has also been completed. Additional research has evaluated alternative methods of underground coal transportation using an entry program that substitutes trackless haulage for belts in subpanels. This work revealed a number of possibilities for improving productivity in underground coal mines. The "SCHED" program was expanded to include the average quality of mine production and is now largely complete.



Research Assistant Uses a Computer Terminal To Facilitate a Study in Mining Design

PLANS FOR THE COMING YEAR – The project will be completed during the coming year, including the writing of the final report and the user's manual for the computer programs.

PERFORMANCE OF DIESEL ENGINES OPERATING ON COAL

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
DOE - $56,104; VPI and SU $5295
9/25/78 - 12/24/79
Principal Investigator - H.P. Marshall

OBJECTIVES – This work concerns the use of coal as a fuel for diesel engines. Large quantities of crude oil could be conserved if the diesel engines used for nonautomotive purposes could be converted to some form of coal. The feasibility of coal mixed with diesel fuel to form slurries rather than coal alone will be demonstrated in this program. The pulverized coal particles will be much smaller (2 μm) than those now used in diesel engines and mixed with diesel fuel to form a partially stable suspension.

RECENT WORK AND ACCOMPLISHMENTS – All work has been preliminary in nature. Instrumentation is being procured and/or constructed. In addition, the slurries intended for use in the experiments are being obtained from the Pittsburgh Energy Technology Center.

PLANS FOR THE COMING YEAR – Experiments will be conducted in which four different slurries will be used as fuels: 20, 35, and 40 percent by weight raw coal and 40 percent by weight solvent refined coal. These experiments will measure changes in diesel engine power and efficiency produced during combustion of each of four different coal-diesel oil slurry fuels relative to operation on regular diesel fuel; measure changes in the production of smoke, NO_x, and SO_x in a diesel engine during combustion of each of four different coal-diesel oil slurry fuels relative to operation on regular diesel fuel; and determine the wear effects produced by the use of coal-diesel oil slurry fuels in a diesel engine.

CHEMISTRY OF DONOR SOLVENT COAL LIQUEFACTION

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
DOE - $308,090; VPI and SU - $183,200
9/1/77 - 8/31/79
Principal Investigators - A.M. Squires, J.G. Dillard, H.C. Dorn, L.T. Taylor

OBJECTIVES – This program is developing and applying analytical techniques to study the chemistry of donor solvent liquefaction of coal, with special emphasis upon regressive reactions that sometimes convert significant portions of the coaly matter to "muck phases"—mesophase and semi-coke. An understanding of the regressive reactions could lead to improvements in coal liquefaction processes; for example, minimizing trouble that sometimes arises from deposits of semi-coke in a donor solvent coal liquefaction reactor and in downstream equipment, or minimizing rate of deactivation of catalytic surfaces, if they are present in the reactor, through formation of deposits upon such surfaces.

RECENT WORK AND ACCOMPLISHMENTS – A batch-stirred microautoclave is preparing samples for examination of both liquefied coaly matter and "muck phases." Preparative separation of the tetrahydrofuran (THF) soluble portions of five solvent refined coals (SRCs) has been accomplished in two ways: using high-performance gel permeation chromatography with Bio-Beads to achieve a separation by molecular size, and using an acid-neutral-base separation that builds upon Sternberg's technique for acid-base separation of asphaltenes. Fractions of SRC have been subjected to quantitative ^{1}H and ^{13}C NMR spectroscopy; that is, samples are studied in which the weight ratio of coaly matter to a reference compound (e.g., hexamethyldisiloxane) is varied systematically. A determination of total H and C should agree with combustion analysis. Association effects in ^{13}C NMR measurements have been seen for heavier fractions of an Amax SRC, and it is likely that as much as 20 to 30 percent of the total carbon was not observed in room-temperature experiments. Measurements at 75°C showed some improvement, but still left doubts. Examination of SRC samples by ^{13}C NMR at elevated temperatures as "melts" was explored up to 200°C. Comparable data, or in most cases better data, have been obtained at four- to five-fold savings in time in respect to experiments for the samples in solution at 32° to 75°C. Trifluoroacetyl chloride and diazotrifluoroethane have proved excellent reagents for introducing a fluorine tag into compounds containing oxygen, nitrogen, and sulfur functional groups in model systems as well as in coaly matter. Detailed model study supports the initial expectation that the ^{19}F NMR chemical shifts (on the order of 2 to 3 ppm) can identify phenolic oxygen, carboxylic oxygen, primary-secondary-tertiary alcohol, amine nitrogen, thiol sulfur, and so forth. In many cases, integration of the reaction product signal relative to a standard ($CFC1_2$-$CFC1_2$) can be used for quantitation. Initial ^{19}F NMR examination of several coaly matter samples is encouraging, and the method has been used to determine a number of heteroatom functionalities in fractions derived from an Amax SRC.

PLANS FOR THE COMING YEAR – Coal liquefaction runs will be made in the microautoclave under conditions leading to a large conversion to pyridine-soluble matter (e.g., at short reaction times or at long times with a good donor solvent), and also under conditions leading to a large yield of "muck phases." Liquefied coaly matter will be separated into fractions and examined by quantitative ^{1}H NMR, by high-temperature quantitative ^{13}C NMR, and, following trifluoroacetylation, by quantitative ^{19}F NMR. The feasibility of placing ^{1}H NMR spectroscopy on-line with high-performance liquid chromatography will be explored.

THERMAL STABILITY OF FERRITIC ALLOYS FOR FOSSIL FUEL PROCESSING SYSTEMS

UNIVERSITY OF WASHINGTON
DOE - $48,483
9/1/78 - 8/31/80
Principal Investigator - D.H. Polonis

OBJECTIVES – This program is evaluating the metallurgical stability of several promising ferritic alloy steels at temperatures up to 1000°C. The influence of aluminum and hafnium additions on the thermal stability of Fe-Cr alloys containing less than 22 percent Cr is of special interest. The program will attempt to determine the effects of composition and temperature on the kinetics of instability.

RECENT WORK AND ACCOMPLISHMENTS – The work performed so far has been limited to the acquisition of alloys and setting up of experimental facilities. Contact has been established with Lockheed Research Laboratories (where related studies on sulfidation-resistant ferritic alloys are ongoing), and they have supplied several alloys for the thermal stability studies. A standard potentiometric method is being set up for the measurement of electrical resistance. The technique involves measuring the voltage drop across the specimen and across a standard resistor. The accuracy of the resistance measurements is expected to be better than ±0.01 percent through the use of a current reversal procedure to eliminate the effects of thermal e.m.f. The apparatus is being checked out, and preliminary aging experiments will begin next month.

PLANS FOR THE COMING YEAR – Several additional model alloy compositions have been selected for investigation and will be prepared. A program of aging experiments is being initiated. The influence of Al and Hf additions on the thermal stability of ferritic alloys will be examined by employing electrical resistance measurements, X-ray analysis, and microscopy, including SEM techniques. Solution-treated alloys will be aged at several temperatures up to approximately 1000°C with special focus on the range 450° to 500°C, which has been identified as an embrittlement region in ferritic stainless steels. Attempts will be made to determine the influence of alloy composition and aging temperature on the kinetics of the reaction and to develop quantitative descriptions of thermal instability from the electrical resistance measurements and X-ray diffraction results. The thermal stability of the model alloys used in this program will be compared with the results for Fe-Cr commercial alloys.

FATE OF FUEL-SULFUR IN BACKMIXED CONTINUOUS COMBUSTION

WASHINGTON STATE UNIVERSITY
DOE - $118,798; Washington State U - $6040
2/1/76 - 8/31/79
Principal Investigators - P.C. Malte, W.L. Grosshandler

OBJECTIVES — Laboratory experiments are conducted to provide a data base on sulfur compounds that form in utility and industrial combustors that burn pulverized coal. Such combustors use backmixing to stabilize the flame. This research is designed to overcome deficiencies in data in the program area. Its payoff will be a better understanding of sulfur species in combustion systems so that utility and industrial boilers can be designed to minimize the deleterious effects of sulfur on system corrosion and on pollutant emissions. Specific objectives are the kinetics of SO_3 formation; systematic measurement of the sulfurous products of fuel-rich combustion (i.e., H_2S, COS, CS_2, mercaptans, and polycyclic hydrocarbons); and measurements of the composition and kinetics of the volatilization of sulfur from pulverized coal and from model sulfur compounds (i.e., thiophene).

RECENT WORK AND ACCOMPLISHMENTS — Production data have been obtained in a jet-stirred Longwell reactor operated on several fuels (C_3H_8, CH_4, C_2H_2, CO/H_2) and doped with several sulfur additives (H_2S, SO_2, and thiophene). Thiophene, C_4H_4S, is a *model compound for organic* sulfur in coal. The reactor has been systematically varied over combustion temperature, fuel/air ratio, and residence time. The results indicate that SO_2 is the dominant sulfur product, even at quite fuel-rich conditions (i.e., 70 percent excess fuel); however, the secondary sulfur products H_2S and CS_2 are observed at yields of 2 to 10 percent of the total sulfur in fuel-rich combustion. In the absence of hydrocarbons, H_2S is the only secondary sulfur product. With hydrocarbon fuels, peak H_2S levels are reached at about 30 percent excess fuel. At richer conditions, the secondary sulfur product is primarily CS_2, which appears to form because of the reaction between sulfur fragments and unburned hydrocarbons. The decomposition rate of thiophene under fuel-rich combustion conditions has also been determined. Production experiments in a backmixed pulverized coal burner are underway. Sulfur yields from the volatilized matter are being measured at a range of locations in the burner. Variables are fuel-air ratio, coal type (Utah, Washington, North Dakota), and residence time.

PLANS FOR THE COMING YEAR — The research is scheduled for completion in the coming year. Data yet to be obtained include the SO_3 measurements, and initial optical measurements of sulfur-tree radicals.

STRUCTURAL MECHANICS SIMULATIONS ASSOCIATED WITH UNDERGROUND COAL GASIFICATION

WEST VIRGINIA UNIVERSITY AND OHIO STATE UNIVERSITY
DOE - $155,517; West Virginia U/Ohio State U - $9568
5/1/76 - 4/30/79
Principal Investigator - S.H. Advani

OBJECTIVES — The goal of this research is to develop predictive structural model simulations of the displacements, strains, stresses, and permeabilities associated with in situ coal conversion. This simulation is a satellite of the overall Morgantown Energy Technology Center program in the areas of reaction kinetics, fluid flow, heat transfer, and structural mechanics for supplementing field testing being conducted at Pricetown, West Virginia. The analytical results will provide design criteria and fundamental insight on roof collapse, surface subsidence, cavity configuration, flame front stability, and variation of coal permeability.

RECENT WORK AND ACCOMPLISHMENTS – Temperature, stress, roof collapse, and subsidence evaluation using finite element models for several in situ combustion configurations have been completed. Fracture and permeability characterization of Pittsburgh coal is being pursued.

PLANS FOR THE COMING YEAR – Investigations will include refinement of the finite element models for design applications. In addition, fracture penetration considerations in the overburden layer with the effects of thermal loading, in situ stresses, and pressure are being pursued.

COAL MINERALS BIBLIOGRAPHY

WEST VIRGINIA UNIVERSITY
DOE - $83,200
6/15/77 - 6/14/78
Principal Investigators - D.J. Akers, B.G. McMillan

OBJECTIVES – The objective is to survey and compile into a critical and annotated bibliography available literature on: the solid inorganic constituents associated with coal (extraneous mineral matter), the mineral matter found within the coal matrix (inherent mineral matter), and mineral matter found in coal byproducts produced from coal extraction, preparation, gasification, combustion, and liquefaction processes. The purpose of the bibliography on coal minerals is to provide an updated data base for the ongoing and planned research at the Coal Research Bureau on the effects of minerals on coal utilization and conversion processes and on coal waste utilization, and for use by other researchers who are involved in all phases of coal handling and processing and who will need information on minerals in coal.

RECENT WORK AND ACCOMPLISHMENTS – A 222 page report entitled *Coal Minerals Bibliography* was submitted in August 1978 to the Technical Information Center, Oak Ridge, Tennessee, for publication. There has been a second publication based on information gained during this project: *Uranium in Coal and Carbonaceous Rocks in the United States and Canada: An Annotated Bibliography*, Coal Research Bureau Technical Report No. 160, College of Mineral and Energy Resources, West Virginia University, Morgantown, West Virginia, 1978.

PLANS FOR THE COMING YEAR – This contract was completed during the fiscal year.

DESIGN OF HIGH-PRESSURE ROTARY PISTON COAL FEEDER

WEST VIRGINIA UNIVERSITY
DOE - $135,360; West Virginia U - $8412
10/74 - 9/79
Principal Investigator - H.T. Gencsoy

OBJECTIVES – The objective is the design of a dry coal feeder with discharge capabilities of 1500 psig and 350°F. The critical design problems are the rotary-piston mechanism, and lubrication, wear, and sealing of feeder components. The initial design in Phase I is for 100-psig discharge pressure at 350°F, with a feed capacity of 200 to 1000 lb/hr. Design problems associated with the rotary feeder must be solved at these modest conditions before higher pressures and flows can be achieved. Phase II consists of fabrication and testing of the prototype pump. The important step in all gasification processes is the feeding of coal from atmospheric pressure into gasifiers operating at pressures up to 1500 psig. For coal gasification to become a commercial reality, feed systems that provide continuous and reliable high flow rates of feedstock must be developed. They must also be built at reasonable capital costs without sacrificing overall process efficiency. The rotary-piston coal feeder seems to meet these criteria.

RECENT WORK AND ACCOMPLISHMENTS — In Phase I, a feeder with 100-psig discharge capability was designed, and all related problems, such as lubrication, wear, and seals, were investigated. In Phase II, a prototype feeder is being built for seal testing only. Special wear-compensating-type seals were developed for this application. Arrangements are being made for their fabrication.

PLANS FOR THE COMING YEAR — Fabrication of the feeder components will be completed, and the prototype test unit assembled for testing. Feasibility and development capabilities of the new seals will be evaluated first under operating pressure conditions only. Seal wear and gas leakage rates will be investigated; if necessary, various other design concepts will be investigated for successful seal operation. Following the seal testing, a complete prototype feeder will be built and tested for general performance of its various components, such as bearings, cams, cam followers, and linear ball bushings.

ASH REMOVAL FROM COAL-DERIVED LIQUIDS

WEST VIRGINIA UNIVERSITY
DOE - $232,941
4/1/76 - 6/30/80
Principal Investigator - J.D. Henry

OBJECTIVES — The objective is to demonstrate the feasibility of using a dispersed water phase to remove mineral matter from coal-derived liquids. The process involves either the extraction of the hydrophobic-coated mineral matter particles into an aqueous phase or the collection of the particles at the interface. The water phase is subsequently removed by electrical coalescence. Specific research objectives are: identification of surface active agents that will promote the distribution or collection of asphaltene-coated mineral matter from SRC filter feed to an aqueous interface or phase, the influence of aqueous phase pH, correlation of dispersed phase experiments with solvent refined coal (SRC) filter feed with three-phase contact angle measurements, the extent of particle removal from the oil phase with sequential or staged water addition, and the experiments to identify parameters controlling the performance of electrical coalescence.

RECENT WORK AND ACCOMPLISHMENTS — Surfactant wetting agents have been identified that effectively promote the collection of asphaltic-coated mineral matter particles at water droplet interfaces. A striking correlation has been obtained between the dispersed phase experiments and three-phase contact angle measurements obtained on surfaces cast from asphaltic-coated mineral matter that has been filtered from SRC filter feed. Three-phase contact angle measurements can be used both to screen new candidate surface active wetting agents and to evaluate the influence of parameters such as concentration. The aqueous phase pH has a pronounced effect on the wetting characteristics of asphaltic-coated mineral matter particles. Increasing the pH to around 10 to 11 reduces the three-phase contact angle to 30 degrees. In addition, increases in the aqueous phase pH lead to a corresponding increase in the particle removal from SRC filter feed as evidenced by the basic sediment and water data. The major conclusion is that it is possible to alter the wetting characteristics of asphaltic-coated mineral particles by aqueous phase pH adjustment without the addition of surfactant wetting agents, which would reduce the initial surfactant costs, and also would involve a process alternative that would be more appropriate for recycling water after removal by electrical coalescence and final particulate removal from the water phase. Sequential or staged water addition to SRC filter feed can be used to increase the removal of mineral matter to an arbitrary high level. Early data show that an excess of 95 percent removal of mineral matter is achieved with three sequential additions. A detailed mechanistic study of electrical coalescence has been conducted. An improved electrical coalescer configuration (documented in a patent disclosure to DOE) involves the combination of both AC and DC electric fields and the use of water wetted DC electrodes that will promote droplet collection.

PLANS FOR THE COMING YEAR – Many of the dispersed phase B.S.&W. experiments and contact angle measurements have been limited to temperatures of 190° to 200°F. Preliminary experiments indicate that the wetting characteristics of particles is not adversely affected at temperatures as high as 400°F. An experimental system for high-temperature dispersed phased experiments will be evaluated, involving a batch three-phase contacting device that can be used in conjunction with X-ray photographs to observe the phase separation. This system can be operated at temperatures as high as 500° to 600°F. In addition, the three-phase contact angle goniometer is being adapted for high-temperature operation. Various process alternatives or configurations for exploiting mineral matter particle collection at a water interface will be evaluated also.

UTILIZATION OF COAL-ASSOCIATED MINERALS

WEST VIRGINIA UNIVERSITY
DOE - $378,000; West Virginia U - $70,000
9/25/77 - 9/24/80
Principal Investigator - J.W. Leonard

OBJECTIVES – The purpose is to examine the recovery and utilization of valuable raw materials and byproducts from coal preparation, conversion, and combustion wastes, and thereby propose or provide methods to enhance commercial acceptance of these processes. Specific studies will focus on wastes from the BIGAS processes at Homer City, Pa., and two coal preparation plants in West Virginia and Pennsylvania.

RECENT WORK AND ACCOMPLISHMENTS – Representative samples of plant feed coal, as well as washed coal and refuse, were obtained from a preparation plant cleaning Pittsburgh seam coal. These samples are being analyzed for chemical and physical properties. Also representative samples of feed coal, feed limestone, "spent" limestone bed material, and flyash from the carbon burnoff cell were obtained from the Pope, Evans and Robbins limestone fluidized-bed process at Rivesville, West Virginia. These samples are also being analyzed for chemical and physical properties. All samples are stored in an inert gas atmosphere to prevent oxidation. Research is underway to determine if the "spent" limestone bed material from the Pope, Evans and Robbins fluidized-bed process can be used in flyash-based fired structural products. Equipment used in the laboratory production and testing of mineral wool has been reconditioned, and several samples of mineral wool have been produced from coal waste materials from the Eastern and Central United States. Methods of physical property testing of the new products by comparison with commercial drawn glass insulation for corrosion resistance, heat conductance, and odor retention are being investigated and evaluated.

PLANS FOR THE COMING YEAR – Samples of plant feed as well as washed coal and refuse will be obtained from a preparation plant cleaning coal from the Allegheny formation. Analyses of these samples will be made for chemical and physical properties. It is planned that samples from six process sites will be obtained during a sustained, steady-state run of the BIGAS process at Homer City, Pennsylvania. Work will continue in an effort to use samples of waste byproducts to produce structural materials that show promise of commercial acceptance and characteristics equal or superior to existing products. New and/or improved processes for the utilization of coal-derived solid wastes will be proposed and investigated.

COAL-ASSOCIATED WASTES FROM COAL MINING, PROCESSING, AND UTILIZATION

WEST VIRGINIA UNIVERSITY
DOE - $1,231,290; West Virginia U - $27,000
4/2/72 - 9/30/79
Principal Investigator - J.W. Leonard

OBJECTIVES – The objectives include the chemical and physical characterization of coal and coal wastes, the investigation of several potential waste utilization processes and/or disposal methods, and the examination of their possible environmental impact upon the Nation. Among the wastes investigated are byproducts from coal cleaning and utilization such as gob, coal fines, "modified flyashes," alkaline earth fluidized-bed combustion products, coal ashes, and other wastes that arise from coal-associated processes

RECENT WORK AND ACCOMPLISHMENTS – All sample processing, characterization, and experimental testing have been completed. Data analysis, verification, and evaluation are nearing completion, and preparation of the final contract report has begun. Two sections have been submitted to DOE in draft form for examination and comment. The first section pertains to the characterization of bituminous coal refuse from cleaning and preparation plants located in nine coal-producing districts of the United States (which account for nearly 75 percent of the Nation's bituminous coal production). A brief description of the coals and cleaning processes for each district is presented along with the characterization of an "average" or composite refuse for that district. Characterization data for individual samples within each district include chemical composition, proximate analysis, sulfur, loss on ignition (LOI), BTU, ash fusion properties, water solubility, bulk density, and size distributions presented in tabular form so that comparisons can be made of refuse materials within and between districts. The second section pertains to the Sulfurtain Process, which involves a possible method of retaining in the ash product during combustion a major portion of the sulfur present in coal. Limestone and other similar material are used as adsorptive agents, but this process differs from previous studies in that an intimate contact of the coal and limestone particles is achieved prior to combustion. Laboratory tests were performed using noncompliance (high-sulfur) steam coals and coal refuse fines with very promising results (up to

95 percent retention of the sulfur). An attempt to use the process in an existing power plant proved unsuccessful possibly because of improper mixing resulting in a lack of intimate contact between particles. This research will continue under other sponsorship. Other research efforts included the selective precipitation of metal constituents from acid mine drainage during the neutralization process, the production of aerated concrete from limestone fluidized-bed combustor refuse, and the production of construction material from conventional bituminous coal ashes and from "modified" ashes.

PLANS FOR THE COMING YEAR — Data verification and evaluation will be concluded, and remaining sections of the final report will be completed.

EFFECTS OF MINERALS ON COAL BENEFICIATION PROCESSES

WEST VIRGINIA UNIVERSITY
DOE - $470,537; West Virginia U - $79,992
9/20/77 - 9/19/80
Principal Investigator - J.W. Leonard

OBJECTIVES — The purpose is to determine the effects of coal-associated minerals on conventional coal beneficiation processes and the effects of these processes on the minerals themselves. Characterization of inherent coal mineral matter in the raw feed, clean-coal products, middlings, and refuse from commercial coal preparation plants will be used to determine, for coal minerals: their original forms and distributions in the feed coal; the changes which they undergo during beneficiation; their specific influences on coal cleaning processes; and improved cleaning technology for optimizing coal usage. Commercial preparation plant feed will also be subjected to a number of mineral dressing techniques in the laboratory, including: size classification, gravity separation, tabling, jigging, froth flotation, and cycloning. The work will provide additional characterization of mineral effects on beneficiation for major coal regions where beneficiation technology is essential to marketing in a clean coal.

RECENT WORK AND ACCOMPLISHMENTS — Commercial coal preparation plant feed and products from the Pittsburgh seam (Northern West Virginia), the Pocahontas No. 3 seam (Southern West Virginia), and the Illinois No. 6 seam (Central Illinois) have been sampled and are undergoing physical and chemical characterization. Bulk amounts of incremental beltline samples were collected including raw feed coal, clean coal, refuse, and fines and are being processed and analyzed using a number of techniques for major and minor mineral and elemental distributions. Petrographic techniques have also been used for examining mineral matter and maceral occurrences in sized and laboratory-washed gravity fractions. Analyses of portions of these samples for proximate, ultimate, Btu, sulfur forms, and so forth are being computer coded for statistical analysis of trends and correlations in the data. An evaluation of results from the preliminary processing of raw coal feed through the laboratory-scale cleaning plant has indicated the need for modifications in the laboratory preparation plant equipment. These modifications are being made and when accomplished will permit processing of raw head samples through both a heavy-media circuit and an all-water circuit. In addition to crushing and screening, the facility includes a single-compartment jig washer, a tabling unit, a heavy-media magnetic drum separator, and a froth flotation cell. Information from the initial stages of optimizing this batch-scale operation and analyzing products is still preliminary.

PLANS FOR THE COMING YEAR — It is anticipated that a complete chemical and physical characterization of major parameters for the Pittsburgh and Pocahontas No. 3 feed and product streams will be complete and that a large portion of the Illinois No. 6 sample will be processed. Mineral identification procedures may lag slightly behind, but are being scheduled in this manner to take advantage of the chemical analyses. A combined assessment of mineral matter distributions in beneficiated products and rejects from commercial preparation plants and the laboratory-scale cleaning equipment will be used to extensively examine the beneficiation process and further the assessment of the laboratory-cleaning tests. The determination of the effects of commercial coal-cleaning methods on mineral composition and distribution will be nearing completion. Computer-assisted analysis of all data will be done to determine specific areas for further testing to develop new and improved methods for coal cleaning.

PREDICTION MODEL FOR COMPOSITIONAL CHANGES WITHIN COAL FROM CORE DATA

WEST VIRGINIA UNIVERSITY
DOE - $184,125
6/1/76 - 6/30/79
Principal Investigator - J.J. Renton

OBJECTIVES — The objectives of this study are to establish the systematic variation of the basic compositional parameters within coal on both a local within-a-mine and on a regional scale; statistically evaluate the data to establish interrelationships that my exist between the basic compositional parameters; relate the compositional variability observed within the study coal to other coals; study the modern peat-forming environment and correlate observed compositional variation of coal with the modern depositional environment; and formulate a geochemical-sedimentological model based upon the combined data that will explain the observed compositional variation, as well as permit a degree of compositional prediction based upon limited sampling.

RECENT WORK AND ACCOMPLISHMENTS — The work of the first 2 years was divided into three separate but interrelated phases: regional sedimentological study designed to determine the main factors controlling the area distribution and thickness of the study coal; detailed petrographic study of a local mine to determine whether or not laterally persistent petrographic zones existed within the coal that could be correlated both within the mine as well as between adjacent mines, and also to establish correlations between the basic petrographic parameters (lithotypes and/or macerals) and the basic inorganic components of coal; and detailed study of the inorganic portion of the coal including the systematic stratigraphic and lateral variability of ash, ash mineralogy, sulfur including total pyritic, organic, and sulphate forms, and a detailed study of the pyritic content including size distributions, morphological forms, and maceral associations. All the work outlined in these three phases has been completed and is reported in the form of Masters' theses at West Virginia University.

PLANS FOR THE COMING YEAR — The work of the third year of the study is divided into three basic areas: a compilation of all available data on West Virginia coals (primarily from the data bank of the West Virginia Geological Survey and the Department of Geology) to which the relationships established during the first 2 years will be applied, and statistical correlations established for the study coal will be tested; a study of modern peat-forming environments in which cores will be taken of the peat as well as samplings of the swamp waters and major plants contributing to the peat; and the formulation of the final geochemical-sedimentological model based upon all data.

COAL THERMOLYSIS – A FUNDAMENTAL CHEMICAL KINETICS APPROACH

WEST VIRGINIA UNIVERSITY
DOE - $40,000; West Virginia U - $2784
9/77 - 8/79
Principal Investigator - S.E. Stein

OBJECTIVES – The goal is to gain a firm understanding of key chemical pathways in coal conversion. This program applies a unified experimental and theoretical approach in which rates of products evolution in liquid-phase pyrolysis of coal-related compounds are measured and then interpreted using predictive methods of elementary chemical kinetics. Detailed reaction pathways characteristic of aromatic pyrolysis, along with associated elementary rates, are sought with the aim of application to practical coal conversion processes. Of particular interest are modes of bond rupture, hydrogen transfer and polymerization.

RECENT WORK AND ACCOMPLISHMENTS – Experimental work has focused on liquid-phase thermal decomposition of polyaromatic compounds and mixtures that have a well-defined initial reaction step. Reaction systems are chosen for their potential for elucidation of common reaction pathways and rates in aromatic pyrolysis, and are not intended to directly simulate real processes. A thorough study of 1,2-diphenylethane (DPE) thermolysis from 325° to 450°C is near completion. Conventional chemical "intuition" does not aid in the interpretation of these results since it is generally based on results from reactions under rather mild conditions (<200°C); however, rate estimation methods developed primarily for gas-phase reactions provide useful predictive ability. It is anticipated that in actual coal processes, rate estimation methods must be used to examine kinetics. A detailed mechanism of DPE pyrolysis has emerged, and certain key relative rates have been found. The influence of oxygen-containing functional groups on the kinetics of aromatic pyrolysis is under study. Although pyrolysis of benzophenone/tetralin and benzhydrol/tetralin mixtures leads to several reproducible products, rates of decomposition are highly erratic, and a free radical mechanism seems incapable of explaining the observed kinetics. The behavior of these and related oxygen-containing systems seems to be quite different than their hydrocarbon analogues, and a heterogeneous or ionic mechanism is suspected. Since the oxygen content of coals has a strong relation to its liquefaction characteristics, the elucidation of this type of reaction may be directly relevant to coal thermolysis and is being actively pursued. Studies of DPE, benzyl-phenylether, and diphenyl-disulfide decomposition in tetralin are providing two types of information: first, measured rate parameters for bond scission of these compounds will lead to reliable methods for estimating bond-breaking rates in liquids using available gas-phase data; second, these systems allow an examination of the mode of action of tetralin with free radicals over a wide temperature range (200° to 450°C). These studies provide evidence that free H-atoms are produced in the conversion of tetralin to napthalene.

PLANS FOR THE COMING YEAR – Studies on these chemical systems will be completed and in some cases extended. Special attention will be paid to the kinetics of decomposition of oxygen-containing substances and to the mechanism of hydrogenation by tetralin. A computer simulation of DPE pyrolysis will be completed and comparisons will be made between gas-phase and liquid-phase rate constants with the aim of improving the accuracy of rate constant estimation for coal-related reactions. A quantitative examination of different bond-breaking mechanisms in coal thermolysis will be made for a wide range of chemical structures characteristic of coal and coal products.

OPTIMIZATION STUDIES OF VARIOUS COAL-CONVERSION SYSTEMS

WEST VIRGINIA UNIVERSITY
DOE - $208,173; West Virginia U - $13,878
3/1/76 - 2/28/79
Principal Investigator - C.Y. Wen

OBJECTIVES — The objective is to provide a critical assessment of coal conversion processes, and produce system models for identifying those processes or process steps that are major technical bottlenecks so that either an alternate process can be suggested or particular steps can be replaced. The work includes the establishment of a generalized standard method of comparison using mathematical optimization techniques for evaluating each unit operation found in various coal-conversion processes.

RECENT WORK AND ACCOMPLISHMENTS — A mathematical model has been developed to simulate the Texaco downflow entrained-bed gasifier using coal liquefaction residues and coal-water slurries as feedstocks. Temperature and concentration profiles along the reactor were obtained by solving the material and energy balances and taking into consideration gasification kinetics, transport rates, and hydrodynamics of the gasifier. The results of computation from the proposed model were compared with the experimental pilot plant data. A sensitivity test was performed to assess the importance of the operating parameters used in the gasifier model. Coal dissolution data from laboratories and pilot units of different coal liquefaction processes were analyzed. The conversion of coal to oil via preasphaltene and asphaltene formation was considered to take place in series. Two different reaction stages seem to exist in the coal dissolution reactions. Initially, coal undergoes a fast thermal reaction producing preasphaltene as the predominant product and can be represented by a first-order reaction scheme. Conversion for this reaction is calculated based on the amount of pyridine solubles formed. The rate coefficient is found to follow an Arrhenius-type temperature dependence with an activation energy of 48≅55 kcal/g-mole. In the second stage of coal dissolution, a slower first-order rate expression is proposed in which the preasphaltene is converted to benzene solubles with subsequent rehydrogenation of the coal-derived solvent. A semi-empirical correlation for the dissolution rate coefficient in the second stage reaction is presented that is affected by hydrodynamics of the reaction, temperature, and hydrogen partial pressure. The rate coefficient is found to be practically independent of coal particle size. The rate of hydrogen absorption during coal dissolution has been also modeled by assuming that the gas and liquid phases are in equilibrium at the interface. The overall gas absorption coefficient is correlated in terms of superficial gas velocity.

PLANS FOR THE COMING YEAR — The analysis of coal liquefaction will be extended to include the catalytic effect on product distribution by recycling part of the unfiltered product slurry as in the SRC-II process.

ROLE OF C-CO_2 IN GASIFICATION OF COAL AND CHAR

WEST VIRGINIA UNIVERSITY
DOE - $283,230
8/16/78 - 8/15/81
Principal Investigators - C.Y. Wen, J.T. Sears

OBJECTIVES — This project is designed to support fluid-bed gasifier programs and to develop gasification models in three phases. The first phase is to determine the kinetics of reactions of char in carbon dioxide, steam, carbon monoxide, and other gasification gases; and to evaluate the rate on the basis of char constituents, surface area for reaction, and effect of diffusion. The pressure range is from 0 to 550 psig, and temperatures from 800° to 1700°C. The second phase is to examine coal-char fluid-bed dynamics with respect to bubble size velocity, particle attrition, and elutriation. In the third phase, a fluid-bed gasifier model is to be developed to utilize the results from the first two phases. The model will be tested by a comparison with tests from experiments on a hot fluidized bed.

RECENT WORK AND ACCOMPLISHMENTS – Three study tasks were started: the catalytic effects of CaO and other additives were investigated; a study of reactivity with CO_2 and other gases at temperature and pressure was started to extend the correlation of char-CO_2 reactivity with CaO and char oxygen; and the flow characteristics of coal and char particles are to be investigated in cold fluidized beds. The effects of physical admixing of lime or K_2CO_3 and coal char (200 to 500μ) were investigated and compared with undoped coal char and solution-impregnated coal char. The same rate of reaction of undoped coal char with CO_2 at 900°C was found with an admixture of K_2CO_3 and coal char at 650°C. With CaO admixed, the reactivity is only slightly increased, if at all, when compared with undoped char. A computer model is being developed for pore size and pore area expansion based on an initial pore-size distribution to include diffusional effects. Only initial screening runs to measure bubbling phenomena in a sand/char fluidized bed have been completed for several different bed velocities. Bubble velocity and frequency are measured at various positions in the bed using the LED (light) probe. Operational features for experimental designs have been identified.

PLANS FOR THE COMING YEAR – Plans call for an emphasis on char reactivity studies. The areas to be investigated initially include char-H_2O reactivity at both 1 atm and high pressure, catalytic char reactivity of both impregnated and natural mineral matter, development of surface area and pore distribution with conversion of the above reactions, and measurement of effective diffusivity of gases. The last area needs to be studied to develop a reactivity model to include diffusivity limitations at high reactivities or pressures. Fluidization work will center on development of an experimental procedure and analysis for measuring bubble distribution, velocity, and size in char-fluidized beds with both flat plate and conical grid designs.

CONCENTRATION CELLS FOR COMBUSTION IMPROVEMENT

MARQUETTE UNIVERSITY
DOE - \$50,000; Marquette U - \$19,340
9/1/78 - 8/31/80
Principal Investigator - R.A. Gaggioli

OBJECTIVES – The objective is to establish the feasibility of using zirconia- or ceria-electrolyte oxygen concentration cells to reduce the chemical potential of O_2, prior to its use for combustion or conversion of fossil fuels; in particular, to make an analytic study of the technical feasibility, to carry out a basic economic feasibility study, to conduct a detailed economic feasibility study, and to undertake an experimental study (bench top).

RECENT WORK AND ACCOMPLISHMENTS – Calculations are being made to evaluate the oxygen flow rates and chemical-potential drops through cylindrical ceria electrolytes at open-circuit conditions.

PLANS FOR THE COMING YEAR — It is planned to continue with theoretical calculations determining performance with different values of various system parameters (such as electrolyte thickness and operating temperature) and employing more refined theoretical models for fluid flow, diffusion, and heat transfer both within the cylindrical combustion cell and for external flows. It is also planned to do preliminary experimental studies, employing ceria as electrolyte, burning H_2 and CH_4 with oxygen extracted from air by the combustion within the cell, separated from the N_2 by the ceria.

METAL CATALYZED REACTIONS OF POLYAROMATIC COMPOUNDS

UNIVERSITY OF WISCONSIN-MADISON
DOE - $40,000
8/29/77 - Continuing
Principal Investigator - P.M. Treichel

OBJECTIVES — The goal is to elucidate various types of reactions of fused ring polyaromatic compounds that are complexed to metals. It is believed that the presence of a complexed metal will alter the reactivity of the hydrocarbon in an advantageous fashion, so that such reactions can be used in developing synthetic pathways to significant organic products. The intent is to convert a hydrocarbon raw material into a desired product via metal complex formation and its subsequent reaction or derivatization. It is presumed, of course, that the same conversion is not possible directly either because of kinetic or perhaps thermodynamic factors. For this study, model systems are to be used involving fused ring aromatic hydrocarbons of various complexity. Obviously a longer term goal is the use of very large polyaromatic molecules and eventual graphitic materials themselves for this study since it is only with such raw materials that real significance of this work can be realized. Ultimately, it is hoped that processes will be defined that will allow various coal-based products to be used as carbon containing raw materials in place of petroleum, since use of the latter is going to be limited both by availability and by cost factors.

RECENT WORK AND ACCOMPLISHMENTS — The syntheses of metal complexes of polycyclic aromatics is the first problem to be faced. Before this work was initiated there were, in fact, very few such complexes known but some success has been achieved. Attempts have been made to synthesize several other types of metal complexes, but they have not yet been successful. Some of these synthetic routes reported were not already known; in particular the ruthenium complex synthesis is of interest since it appears to provide a way to prepare a wide range of complexes having two dissimilar arene ligands. Initial exploration of the reaction chemistry of these complexes has begun. This work is as yet incomplete but preliminary evidence in several areas is quite promising; for example, some information has been obtained on the relationship between acenaphthene and acenaphthalene complexes of metals. Reduction of the precursor by 2-electron addition gives an aromatic stabilized dianion that on protanation gives the product. This result is exciting because of its potential for the electrochemical hydrogenation of the edge of a graphitic material. Work is underway to determine the stereochemistry of this reaction (relative to the metal). Also underway are attempts to carry out alkylations, carbonylations, and so forth in these systems. Preliminary attempts have been made to halogenate the double bond in this species also. So far products of this reaction have eluded identification. Electrochemical reductions of some of the other complexes have been investigated. These compounds reduce at a relatively low potential but the products of reduction are not stable and have presented difficulties in characterization. Substitution reactions on the arene nucleus with reagents such as alkyl-lithium compounds have not been successful. Some other interesting work on electrochemical reductions and oxidations has appeared. This work is entirely on mono-ring complexes, but success there indicates that this work is moving in the right direction.

PLANS FOR THE COMING YEAR – Some headway has been made in this project; a number of new complexes have been prepared, and a study of the reactivity of these species is underway. A continued and more concentrated effort will be directed to the reaction chemistry of these metal complexes, with the effect of the metal on various reactions a major concern. The displacement or migration of the coordination site of a metal is an important aspect of the overall scheme, and it is important to determine the feasibility.

IRON-INDUCED DEACTIVATION OF NICKEL METHANATION CATALYSTS

UNIVERSITY OF WISCONSIN-MADISON
DOE - $75,600
9/15/78 - 9/15/80
Principal Investigator - J.A. Dumesic

OBJECTIVES – The deactivation of Raney nickel and supported nickel methanation catalysts resulting from iron carbonyl adsorption on and incorporation into the catalyst is being studied using chemical kinetics, dynamic adsorption measurements and in situ spectroscopy. The objectives are to determine the partitioning of the iron between the various components of the catalyst and the relative importance of the different deactivation modes (e.g., iron-nickel alloy formation, iron-induced carbon deposition on the nickel or on the support), to study the effect of process variables on these deactivation rates, and to determine the susceptibility of different nickel catalysts to iron-induced deactivation.

RECENT WORK AND ACCOMPLISHMENTS – Research effort on this project to date has primarily involved the construction of specialized equipment and the preliminary study of iron carbonyl adsorption and decomposition on solid surfaces. Nearly completed is the construction of a high pressure (~70 atm) methanation reactor system that is compatible with the collection of ^{57}Fe Mossbauer spectra under these reaction conditions. The significance of this system is that it will allow a direct comparison of the catalyst deactivation kinetics with the chemical state and distribution of iron on different nickel catalysts under commercially important reaction conditions. The extent of iron carbonyl adsorption and decomposition on solid surfaces is now being studied using a recently constructed apparatus that combines volumetric gas adsorption techniques with Mossbauer spectroscopy. These experiments are designed to probe the specificity of the iron carbonyl interaction with different types of surface sites. Preliminary experiments have shown that the carbonyl adsorbs only weakly on carbon surfaces followed by the formation of highly dispersed iron clusters upon heating to temperatures above 100°C.

PLANS FOR THE COMING YEAR – Existing equipment will be used to study the iron-induced deactivation of nickel methanation catalysts. Controlled pulses of iron carbonyl will be injected into the methanation reactor feed, while Mossbauer spectra and methanation reaction kinetics are being collected. In this manner, the amount of iron present on the catalyst, the location and chemical state of this iron, and the catalytic activity of the sample will be simultaneously determined and correlated. Studies of the specific interaction of iron carbonyl with nickel, carbon, and various oxide supports will also continue. Finally, the chemical state of the nickel in partially deactivated catalysts will be probed under methanation reaction conditions using magnetic susceptibility, and the rate of coke deposition will be studied using microbalance techniques.

COAL BURNING RATE STUDIES

UNIVERSITY OF WISCONSIN-MADISON
DOE - $49,700
9/1/78 - 8/31/80
Principal Investigator - K. W. Ragland

OBJECTIVES — Data on the burning rate of coal particles in a fluidized-bed combustor will be obtained and used to establish a burning rate equation for modeling the performance of a fluidized-bed combustor. The change of size distribution and density of the coal particles during combustion will be examined, and conditions that reduce unburned carbon carryover into the flue gas will be investigated. This information will be useful for modeling coal/ash particulate emissions from fluidized-bed combustors.

RECENT WORK AND ACCOMPLISHMENTS — A 6-in.-diameter quartz-walled fluidized-bed combustor has been designed and constructed. A 24-kw air pre-heater has been designed and built, and is undergoing testing. It is designed to deliver up to 30 scfm at temperatures up to 1600°F. Air flows over 12 silicon-carbide electrodes (3/4-in.-diameter by 24-in.-long with a 12-in. hot section) heated by a direct current. The electrodes are inserted into a 1-in. by 12-in. rectangular duct made of high-temperature castable refractory. The duct then converts to 6-in. diameter to match up with the air injector plate made of 444 stainless steel with 1/16-in.-diameter drilled holes. The quartz tube is attached to the injector plate by means of a retaining ring through which nitrogen quench gas may be introduced into the bed. The combustion tests will be started once the heater tests are completed.

PLANS FOR THE COMING YEAR — Combustion tests on bituminous, subbituminous, and lignite coal will be conducted. Coal particle sizes from 1 to 9 mm, bed temperatures from 1300° to 1600°F, and oxygen concentrations from 5 to 21 percent will be investigated. A batch of 10 nearly identical coal particles will be introduced into a hot inert bed for a known time. The bed will be rapidly quenched and dumped, and the coal particles separated and analyzed. Tests on the particulate emissions will be conducted during the second year.

PARTICULATE REMOVAL BY SELF-AGGLOMERATION IN A CYCLONE

UNIVERSITY OF WISCONSIN-MILWAUKEE
DOE - $40,000; Wisconsin U - $27,000
9/1/77 - 8/31/79
Principal Investigator - K.C. Tsao

OBJECTIVES — The objective is to investigate coal-ash particulate removal through a multiple inlet, multi-pass cyclone operated near ash fusion temperature. Under the centrifugal action, partially molten ash particles will impact, adhere, and agglomerate into greater size and then will be separated out from the main gas stream. High-temperature flue gas, as produced either from fluidized-bed combustion or from coal gasification, will be cleaned to an acceptable degree for safe operation in a combined gas-steam turbine power plant that not only offers the highest thermal performance in coal utilization, but also provides a cleaner environment. This program is concentrated on the practicability of the hardware design and performance, and the development of analytical models to identify the engineering parameters such as temperature, flue velocity, and particle size that would affect the agglomeration process.

RECENT WORK AND ACCOMPLISHMENTS – A mathematical model describing the probability of particle collisions, adhesions, and agglomeration was constructed to estimate the rate of agglomeration process. Comparison of the collection efficiency with or without agglomeration at high temperature is being computed. The model predicts an increase in collection efficiency from 5.37 to 6.36 percent for 1-μ-diameter particles, from 19.81 to 36.69 percent for 2-μ-diameter particles, from 75 to 89.21 percent for 5-μ-diameter particles and 99.5 to 99.76 percent for 10-μ-diameter particles. The overall relative increase of collection efficiency for submicron particles is on the order of 18.4 to 85 percent. Laboratory verification of the analytical results and initial 11 experiment test runs indicate: the agglomeration of particles does exist when cyclone temperature is operated at 1850°F; numerous agglomerated particles have been observed and bond together when the cyclone is operated at 2150°F; microscopic examination of particles sampled from discharge stream shows 85 percent of the collected particles are less than 4μ; with input loadings of 26.93 and 15.82 gr/ft^3 of gas flow, the output dust loadings are reduced to 4.929 and 0.895 gr/ft^3. Coal-ash agglomeration phenomena was also studied in a static furnace. The effect of furnace temperature and duration of exposure have profound influence on coal-ash agglomeration process.

PLANS FOR THE COMING YEAR – Extensive experimental data gathering is being scheduled. Microscopic examination on surface bonding phenomena will be attempted. Cycle efficiency for multi-inlet operation for two different particle sizes in collision will be tested. Correlation of cyclone operating conditions on the collection efficiency will be constructed. The technical assessment applying the high-temperature cyclone for hot-gas cleaning should be completed.

EFFECT OF SOLVENT ON COAL LIQUEFACTION

UNIVERSITY OF WYOMING
DOE - $298,135; Wyoming U - $41,839
5/1/76 - 1/31/79
Principal Investigators - H.F. Silver, R.J. Aurtubise

OBJECTIVES – The objective is to determine what solvent properties enhance the liquefaction of coal.

RECENT WORK AND ACCOMPLISHMENTS – To liquefy Wyodak coal in a stirred-batch reactor under a single set of reactor operating conditions, 25 solvents of varying hydrogen donor capacity and boiling range have been prepared and 9 Wyodak coal-derived solvents have been used. Preliminary results indicate that there is a difference in the effect of solvents studied on the extent of coal liquefaction, asphaltene production, and nitrogen removal. Although there seems to be a trend of increasing solvent effectiveness with increasing solvent boiling range, it appears that more than one solvent property will be required to produce a statistically significant correlation. Work is being directed toward determining physical properties, such as solubility parameters and volumetric average boiling points, as well as chemical properties of the 25 solvents. A quantitative method has been developed for determining tetralin and napthalene in the solvents. A chromatographic correlation factor for high-performance liquid chromatography has been developed that allows speculation on structure and retention volumes of hydroaromatics and polycyclic aromatic hydrocarbons isolated from recycle solvents. Separation, characterization, and identification methods have been developed for monophenols and speculation of the identity of alkylphenols in recycle solvents using open-column chromatography and high-performance liquid chromatography. Procedures have also been developed to determine the classes of nitrogen compounds in solvents and SRC. Preliminary results indicate a high percentage of quinoline-type nitrogen compounds in coal liquids.

PLANS FOR THE COMING YEAR – Work is being directed toward duplicating liquefaction results using the 13 solvents derived from coals other than Wyodak coal. The results of this work, along with measurements of the properties of these solvents, will be used in an attempt to correlate solvent effectiveness. The effect of the addition of mineral-matter-free SRC fractions on solvent effectiveness as well as the relationship between reactor operating conditions and solvent effectiveness may be studied.

WASTE-HEAT RECOVERY BY DESICCANT-BASED POWER GENERATION

UNIVERSITY OF STRATHCLYDE
DOE - $36,700; Strathclyde U - $8560
9/1/78 - 8/31/80
Principal Investigator - J. McKelvie

OBJECTIVES – The purpose is to examine the potential of novel methods of utilizing desiccant-stored energy as a means of recovering waste-heat from fossil-fired power stations. The study will evaluate these desiccant-based systems in terms of mechanical efficiency and economic viability, and will then attempt to optimize an arrangement in which the desiccant is partly regenerated by waste-heat of typical grade. The effects (on the overall generating efficiency and economics) of the use of higher-grade pass-out steam as a regenerating medium will also be examined.

RECENT WORK AND ACCOMPLISHMENTS – Preliminary work has centered on a survey to evaluate the suitability of various desiccants in terms of desirable physical properties, environmental compatibility, and price level. Calcium chloride has been settled upon provisionally as the best compromise. The evaluation has confirmed the behavior of desiccants generally at temperatures up to 250°C to conform to the essential requirements, and moreover, and importantly, has indicated that at these higher temperatures the rate of desiccation is very much greater for desiccant of given condition in air of a given relative humidity. Mathematical description of the behavior of calcium chloride has been set up, and a computer modeling of a desiccant-fueled power cycle has commenced.

PLANS FOR THE COMING YEAR – Once a satisfactory computer-model has been set up, the effects of changes in the power-cycle steps will be studied together with changes in desiccant inlet condition. Data on the atmospheric regeneration of desiccant will be collated and built into a model of the costs of regeneration as a function of climatic conditions. Similarly, models of the costs of regeneration using waste heat and pass-out steam will be built up. The above models together with costs of relevant materials-handling plant and turbo-machinery will be combined to provide a model that will output the optimum design parameters for a generating station combining fossil-fueled with desiccant-based power plant under different climatic conditions.

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ABBREVIATIONS AND ACRONYMS

A

A	ampere
AAG	agglomerating ash gasifier
AAS	atomic absorption spectroscopy
ABCT	autotrack bridge conveyor train
AC	alternating current
ACES	atmospheric combustion exhaust simulator
acfh	actual cubic feet per hour
ACGIH	American Conference of Government-Industrial Hygienists
ADARS	automatic data logging and data reduction system
AE	architect and engineer
AEDC	Arnold Engineering Development Center
AEP	American Electric Power
AERL	Avco Everett Research Laboratory Inc.
AES	atomic emission spectroscopy, Auger electron spectrometer, automated extraction system
AFBC	atmospheric fluidized-bed combustion
AGA	American Gas Association
AID	automatic interaction detection
AMRC	Albany Metallurgy Research Center
ANFO	ammonium nitrate-fuel oil (blasting agents)
ANL	Argonne National Laboratory
APIK	American Petroleum Institute
ARCCM	automated remote control continuous miner
ART	algebraic reconstuction technique, applicable Russian technology
ASTM	American Society for Testing Materials
atm	atmospheres (of pressure)
atma	atmosphere absolute
ATP	adenosene triphosphate

B

BA	budget authority
BAP	benzo(a)pyrene
bbl	barrel
bbl/cd	barrels per calendar day
bbl/d	barrels per day
bbl/m	barrels per minute
bbl/sd	barrels per stream day
BCA	benzene carboxylic acid
BCR	Bituminous Coal Research, Inc.
B.E.T.	Brenaer, Emmett, and Teller method
BETC	Bartlesville Energy Technology Center
BHTP	bottom-hole treating pressure
BIPS	benzene-insoluble, pyridine-soluble
BMIS	business management information systems
BNL	Brookhaven National Laboratory
BO	Budget Outlay
BOD	biochemical oxygen demand
BOM	Bureau of Mines

bp	boiling point
BSB	blind shaft borer
B.S.&W	basic sediment and water
BTC	Battelle treated coal
Btu	British thermal unit
BTX	benzene, toulene, and xylene
B&W	Babcock and Wilcox
BWE	bucket wheel excavator

C

CAI	conodont alteration index
CAPD	combustion and advanced power develop development
CARS	coherent antistokes Raman scattering
CAS	combustion air system
CBC	carbon burnup cell
CBFDP	clean boiler fuel demonstration plant
CC	coal conversion
CCC	coal combustor for cogeneration
CCG	catalytic coal gasification
CCI	conodont color index
CCP	coal conversion processes
CDIF	Component Development and Integration Facility
CDS	chemical data systems
CEF	chemical explosive fracturing
CEI	Combustion Engineering, Inc.
CERT	constant extension rate
CFB	centrifugal fluidized bed
CFC	contract file card
CFCC	coal-fired combined cycle
CFFC	clean fuel from coal
CFFF	Coal-Fired Flow Facility
CG	chemical grafting
CGA	coal gasification atmospheres
CGCC	coal gasification combined cycle
C-h	candle-hour
CIG	Colorado Interstate Gas Company
CLFS	coal liquids flow system
cm	centimeter
CM	conventional magnet
CMC	carboxymethyl cellulose
cm^3	cubic centimeter
CO$_2$	carbon dioxide
COD	chemical oxygen demand
COE	crude oil equivalent
COED	coal oil energy development (liquefaction process)
COG	coal-oil-gas
CO-H$_2$O	carbon monoxide-water
COM	coal-oil mixture
CONBEC	connected-block effective conductivity
Conoco	Continental Oil Company
Consol	Consolidation Coal Company
COWS	coal/oil/water slurry
cp	centipoise
CPC	Combustion Power Company

cpm	cycles per minute
CPU	Combustion Power Unit
CS	compact specimens
CSD	cross-stroke structural discontinuity
CSMRI	Colorado School of Mines and Research Institute
CSTR	continuous-stirred tank reactor
CTF	Combustion Test Facility
CTIF	Component Test and Integration Facility
CTIU	Component and Test Integration Unit
CUNY	City University of New York
cw	continuous wave
CW	Curtiss-Wright
CY	calendar year
CYNGAS	cyclone gasification numerical simulation

D

db	decibel
DBMS	data base management system
DBTT	ductile to brittle transition temperature
DCW	diagonal conducting wall
DDP	detailed development plan
DE&OT	drilling, exploration, and offshore technology
DFFU	Division of Fossil Fuel Utilization
DOC	Department of Commerce
DOD	Department of Defense
DOE	Department of Energy
DOE	Department of Interior
DPE	dephenylethane
DPP	differential pulse polarography
DPS	dragline production simulation
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DWT	deviated well test

E

EA	Environmental Assessment
EAS	Economic Assessment Service
ECAS	Energy Conversion Alternatives Study
ECP	Engineering Change Proposal
EDP	Environmental Development Plan
EDP	equipment design package
EDS	Exxon Donor Solvent
EDXS	energy-dispersive X-ray spectroscopy
EFB	electrofluidized bed
EGR	enhanced gas recovery
EGSP	Eastern Gas Shales Project
EH&S	Environmental Health & Safety
EIA	Environmental Impact Assessment
EIS	Environmental Impact Statement
emf	electromotive force
EOR	enhanced oil recovery
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ER	environmental reports
ER&E	Exxon Research and Engineering Company
ESCA	electron spectroscopy for chemical analysis

ESP	electrostatic precipitator
ESR	electron spin resonance
ESRG	Energy Systems Research Group
ETC	Energy Technology Center
ETF	Engineering Test Facility

F

F	faraday
°F	degrees Fahrenheit
FBC	fluidized-bed combustion
FBN	fuel-bound nitrogen
FBNML	Francis Bitter National Magnet Laboratory
FCC	fluid catalytic cracking
FDP	free-fall dilute phase
FE	Fossil Energy (Program)
FEARB	Fossil Energy Authorization and Review Board
FGD	flue gas desulfurization
FIMS	field ionization mass spectrometry
FIVTF	Flow-Induced Vibration Test Facility
FMA	Foster-Miller Associates Inc.
FMEA	failure mode and effects analysis
ft	foot, feet
ft^3	cubic feet
ft/sec	feet per second
FWEC	Foster Wheeler Energy Corporation
FY	fiscal year

G

g	gram
GC	gas chromatography
GE	General Electric Company
GFETC	Grand Forks Energy Technology Center
GISP	geotechnically instrumented seafloor probe
GMA	gas metal arc
GPC	gel permeation
GPE	Gas Producing Enterprises, Inc.
gpm	gallons per minute
gr	grain
GRI	Gas Research Institute
GSU	Gulf States Utilities
GRF	Generator Test Facility
GURC	Gulf Universities Research Consortium

H

HAZ	heat-affected-zone
HC	hydrocracking
H-Coal	hydrogenated coal
HDS	hydrodesulfurization
HDT	hydrodenitrogenation
HG	hydrogasification
HGI	Hardgrove Grindability Index
HGMS	high-gradient magnetic separator
HGR	hot-gas recycle
HHV	high heating value
HMF	high mass flux
HMIS	horizontal modified in situ
hp	horsepower

HPDE	high-performance demonstration equipment
hr	hour
HRI	Hydrocarbon Research Inc.
H_2S	hydrogen sulfide
HTHP	high temperature, high pressure
HTRF	Hydraulic Transport Research Facility
HTRI	Heat Transfer Research, Inc.
HTTT	high-temperature turbine technology
HVAB	high volatile A bituminous
hz	Hertz

I

IBG	intermediate-Btu gas
IC	internal combustion
ICAP	induction coupled argon plasma
ICGG	Illinois Coal Gasification Group
I.D.	inside diameter
IEA	International Energy Agency
IGT	Institute of Gas Technology
IITRI	IIT Research Institute
in	inch, inches
IR	infrared
IR&T	International Research and Technology Corporation
ISIP	instantaneous shutin pressure
IVTAN	Institute of High Temperatures (Soviet Union)

J

JANAF	Joint Army, Navy, Air Force

K

KG	kilogauss
kg	kilogram
kh	permeability-thickness
kHz	kilohertz
KTO	Koppers-Totzek oxygen
kv	kilovolt
kw	kilowatt

L

LASL	Los Alamos Scientific Laboratory
lb	pound
LBG	low-Btu gas
LBL	Lawrence Berkeley Laboratory
lb	pound-mass
LBG	laser doppler anemometry
LBL	laser doppler velocimetry
lbm	Laramie Energy Technology Center
LDA	Lawrence Livermore Laboratory
LDV	liquid-metal magnetohydrodynamics
LETC	Laramie Energy Technology Center
LLL	Lawrence Livermore Laboratory
LMMHD	liquid-metal magnetohydrodynamics
LN_2	liquid nitrogen
LNG	liquefied natural gas
LP	linear programming
LPF	linear pocket feeder

LPG	liquefied petroleum gas
LPM	liquid-phase methanation
LRS	laser Raman spectroscopy
LRSD	long-range strategy division
LV	laser velocimetry
LVW	linked vertical well
LWG	longwall generator

M

m	meter
μ	micron
M	thousand
ma	milliampere
MAF	moisture and ash-free
MBC	mobile bridge carrier
M-C	molten-carbonate
MCA	Magnetic Corporation of America
Mcf	thousand cubic feet
MCFC	molten carbonate fuel cell
Mcfd	thousand cubic feet per day
MCMS&T	Montana College of Mineral Science and Technology
md	millidarcy
μd	microday
MERDI	Montana Energy and MHD Research & Development Institute, Inc.
MESA	Mining Enforcement and Safety Administration
METC	Morgantown Energy Technology Center
Mev	million electron volts
MFB	multicell fluidized-bed boiler
MFCD	multiple face continuous drivage
MFSU	mobile field support unit
μg	microgram
MHD	magnetohydrodynamics
MHF	massive hydraulic fracturing
$\mathrm{MH_z}$	megahertz
MICO	micronized coal-oil blade
MIKES	mass analyzed ion kinetic energy spectrometry
MINERS	Mineral Resource Evaluation System
MIS	Management Information System
MIT	Massachusetts Institute of Technology
MIUS	Modular Integrated Utility Systems
MLWG	Memphis Light, Water, and Gas Division
MM	million
MMbbl/d	millions of barrels per day
MOR	modulus of rupture
MPF	micellar polymer flooding
MPPM	Materials-Process-Product Model
MS	mass spectral, mass spectroscopy
MSCG	molten-salt coal gasification
MSHA	Mine Safety and Health Administration
MSP	marine sediment penetrators
MSTF	Molten-Salt Test Facility
MSU	Montana State University
MSW	municipal solid waste

MTCH	Mining Technology Clearing House
Mw	megawatt
Mw_e	megawatt electrical
Mw_t	megawatt thermal
MY	man-year

N

NaCl	sodium chloride
NCB	National Coal Board (England)
NDT	nondestructive testing
NEPA	National Environmental Policy Act
NIOSH	National Institute of Occupational Safety & Health
NL	National Laboratory
NMR	nuclear magnetic resonance
NMSC	National Mine Service Company
NO_x	nitrogen oxides
NPDES	National Pollutant Discharge Elimination System
NRDC	National Research Development Corporation
NSF	National Science Foundation
NSPS	New Source Performance Standards
NTIS	National Technical Information Service

O

OCMHD	open-cycle magnetohydrodynamics
OCR	Office of Coal Research
OCS	Outer Continental Shelf
O.D.	outside diameter
ODE	ordinary differential equation
OFDF	opposed flow diffusion flame
ONR	Office of Naval Research
OPDD	overall plant design description
OPEC	oil producing and exporting countries
OPPA	Office of Program Planning and Analysis
ORC	organic Rankine cycle, Occidental Research Corporation
ORGDP	Oak Ridge Gaseous Diffusion Plant
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OS/IES	on-site/integrated energy systems
OSU	Oklahoma State University

P

Pa	pressure atmosphere
PACES	pressurized air combustion exhaust simulator
PAD	Program Approval Document
PAFC	phosphoric acid fuel cell
PAH	polynuclear aromatic hydrocarbon
PB	packet bed
PBP	packed-bed process
PC	pulverized coal
PCCU	production, collection, conversion, and/or utilization
PCE	plant and capital equipment
PCF	pulverized coal-fired
PCIV	prestressed cast-iron pressure vessel
PCOB	powdered coal-oil blends

PCWS	primary cooling water system
Pd	palladium
PDE	partial differential equation
PDU	process development unit
PEDU	process and equipment development unit
PER	Pope, Evans and Robbins
PETC	Pittsburgh Energy Technology Center
PFB	pressurized fluidized bed
PFBC	pressurized fluidized-bed combustion
PI	petrochemical intermediates
PIC	Petroleum Information Corporation
PM	photomultiplier
PNA	polynuclear aromatic
PNG	petroleum and natural gas
POGO	Power-Oil-Gas-Other
PON	Program Opportunity Notice
ppb	parts per billion
PPD	Project Plan Document
PPHTS	particle precipitating heat transfer service
ppm	parts per million
PRD	prime reference design
PSD	prevention of significant deterioration
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PTFE	polytetrafluoroethylene
PV	pore volume
PVT	pressure-volume-temperature

Q

Quad	10^{15} (quadrillion) Btu's

R

RBR	recirculating-bed reactor
R&D	Research and Development
RD&D	Research, Development, and Demonstration
RDD&C	Research, Development, Demonstration, and Commercialization
RDT&E	Research, Development, Test, and Evaluation
RESPONS	Regional Energy System for the Planning and Optimization of National Scenarios
RF	radio frequency
RFB	rotating fluidized bed
RFP	Request for Proposal
RMC	Reynolds Metals Company
RMP	Ralph M. Parsons Company
rms	root mean square
ROI	Return on Investment
RON	research octane number
rpm	revolutions per minute
RS	recycle solvent
RTD	residence time distribution

S

SA	submerged arc
SAEM	scanning and analyzing electron microscope
SARA	solvents-aromatics-resins-asphaltenes
SC	super conducting

scf	standard cubic feet
scfd	standard cubic feet per day
scfh	standard cubic feet per hour
scfm	standard cubic feet per minute
SCMS	superconducting magnet system
SCOOP	Stage Combustion Operation Optimizer Program
SCPE	sublend pairing with pillar extraction
sd	stream day
SDB	steeply dipping bed
SDD	system design description
SDI	selective dissemination of information
SDL	Spectron Development Laboratories
SDU	study design update
S-E	solid-electrolyte
SEB	Source Evaluation Board
sec	second
SECS	specific solvents chromatography
SEM	scanning electron microscopy
SFME	single-face multiple-entry
S/GFTF	solids/gas flow test facility
SGT	small gas turbine
SL	Sandia Laboratory
SLAT	standard liquefaction activity test
SME	shaped memory effect
SNG	substitute natural gas
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_x	oxides of sulfur
SOA	state-of-the-art
SOG	steam-oxygen gasifier
SR	stoichiometric ratio
S-R	Stearns-Roger Engineering Company
SRC	solvent refined coal
SRC-UFO	solvent refined coal-unfiltered oil
SRI	SRI International
SRL	solvent refined lignite
SRSA	Special Research Support Agreement
SS	stainless steel
SSU	subscale unit
STAM	statistical analog monitor
STR	steam reforming
Syngas	synthetic natural gas

T

T	tesla
TBC	thermal barrier coating
TBM	tunnel boring machine
Tcf	trillion cubic feet
TCGP	Texaco Coal Gasification Process
t/cd	tons per calendar day
t/d	tons per day
TDS	total dissolved solids
TESI	Talley Energy Systems, Inc.
TETAS	Total Energy Technology Alternatives Study
TGA	thermogravimetric analysis

THF	tetrahydrofuran
t/hr	tons per hour
TIGER	Thermodynamic Investigation of Gasification Energy Requirements
TILER	Thermodynamic Investigation of Liquefaction Energy Requirements
TIS	technical information source
TOC	total organic carbon
TPO	technical project officer
TR	thermal recovery
TRV	technology readiness vehicle
TSE	test support equipment
TSG	Technology Support Group
TSO	time-sharing option
TTU	Technology Test Unit

U

UCG	underground coal gasification
UCRS	Uniform Contractor Reporting System
UGMHS	underground materials handling simulation
U.K.	United Kingdom
USBM	United States Bureau of Mines
USDA	United States Department of Agriculture
USGS	United States Geological Survey
USS	United States Steel
U.S.S.R.	Union of Soviet Socialist Republics
UTS	ultimate tensile strength
UTSI	University of Tennessee Space Institute
uv	ultraviolet

V

v	volt
V-L-E	vapor-liquid-equilibrium
VRS	vibrational Raman scattering
V-S-E	vapor-solid-equilibrium

W

w	watt
WA	Winkler air
WGA	Wellman-Gallusha air
WGSP	Western Gas Sands Project
w/o	weight percent
WOR	water-to-oil ratio
WRC	Water Resources Council
WRIP	wire rope improvement program

X

XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

GLOSSARY

The intent of this glossary is to give a general definition of terminology as used in this report. A glossary is considered desirable because of the diverse origin of the technology and broad spectrum of potential readers. For more precise and detailed definitions, the reader is referred to *The Annual Book of ASTM Standards* published by the American Society for Testing Materials (ASTM), *Chemical Engineers' Handbook* by R.H. Perry and C.H. Chilton, and *A Dictionary of Mining, Mineral, and Related Terms* published in 1968 by the U.S. Department of the Interior.

Å – Angstrom unit, a unit of length equal to 10^{-10} meters or 10^{-4} microns, generally used as the unit for describing interatomic distances; as an example, the carbon atoms in diamond are 1.5 Å apart.

absorption – the dissolution of a gas in a liquid.

acceptors – calcined carbonates that absorb carbon dioxide evolved during gasification, exothermically.

acid-gas removal – a section of a gas plant where hydrogen sulfide and carbon dioxide are removed from the gas stream.

activated carbon – carbon obtained by carbonization in the absence of air, preferably in a vacuum; has the property of absorbing large quantities of gases, solvent vapors; used also for clarifying liquids.

adiabatic – any process where heat is neither given off nor absorbed.

adsorption – the physical and chemical adherence of a gas to the surface of a solid.

agglomerate – assemblage of ash particles rigidly joined together, as by partial fusion (sintering).

anode carbon – carbon of high purity, usually crystallized to graphite form, widely used in Leclanche cells, in rods for alumina refining, in electric arcs and nuclear reactors.

anthracite coal – any coal containing 86 to 98 percent fixed carbon, on a dry, mineral-matter-free basis.

aromatic hydrocarbon – an unsaturated cyclic hydrocarbon containing one or more six-carbon rings.

ash – theoretically, the inorganic salts contained in coal; practically, the residue from the combustion of dried coal that has been burned at 1,380°F.

autoclave – a vessel, constructed of thick-walled steel (alloy steel or nickel alloys), for carrying out chemical reactions under pressure and at high temperatures.

bench-scale unit – a small-scale laboratory unit for testing process concepts and operating criteria as a first step in the evaluation of a process.

binder – carbon products, tars, etc., used to impart cohesion to the body to be formed; a coal-extract binder may be used to prepare formed-coke pellets from noncoking coals.

bituminous coal – a broad class of coals containing 46 to 86 percent fixed carbon and 20 to 40 percent volatile matter.

blow down – the removal of liquids from a process vessel by the application of pressure.

bottoming cycle – the lower temperature thermodynamic power cycle of a combined-cycle system.

Btu – British thermal unit, the quantity of energy required to raise the temperature of 1 lb of water 1°F.

BTX – benzene, toluene, xylene; aromatic hydrocarbons; toluene is methyl-benzene, xylene is dimethyl benzene.

caking – the softening and agglomeration of coal as a result of the application of heat.

calcine – to heat a solid to a high temperature to cause the decomposition of hydrates and carbonates.

carbon fiber – very fine filaments about 8 microns in diameter that are used in composite materials, being bound with resins.

carbonization – the destructive distillation of coal in the absence of air accompanied by the formation of char (coke), liquid (tar), and gaseous products.

catalyst – a substance that accelerates the rate of a chemical reaction without itself undergoing a permanent chemical change.

centrifuge – an apparatus rotating at high speed to separate solids from liquids, e.g., undissolved residue from coal solution in the SRC process.

char – the solid residue from coal after the removal of moisture and volatile matter, i.e., essentially ash plus fixed carbon.

closed cycle – a thermodynamic power cycle in which the working fluid is recycled.

coal – a natural solid material consisting of amorphous elemental carbon with various amounts of organic and inorganic compounds.

coke – a solid consisting primarily of amorphous carbon having certain properties of strength, cell structure, and minimum impurities, and manufactured by the thermal decomposition of petroleum residues and certain types of coal.

coke breeze – coke particles smaller than 1/2 inch.

combined cycle – two sequential thermodynamic power conversion systems operating at different temperatures.

combustion gas – gas formed by the rapid oxidation of coal, e.g., burning.

combustor – a vessel in which combustion of gaseous products from a fuel takes place by the chemical union of oxygen with the gas.

coupon – a polished metal strip used to measure the rate of corrosion of the metal in a specific gaseous or liquid environment.

cracking – the partial decomposition of high-molecular-weight organic compounds into lower-molecular-weight compounds, generally as a result of high temperatures.

crude gas – gas produced in a gasifier containing a wide range of impurities, also known as offgas.

cyclone separator – essentially a settling chamber to separate solid particles from a gas, in which gravitational acceleration is replaced by centrifugal acceleration.

degasification – a process for draining naturally occurring methane from coal seams.
delayed coking – a process whereby coal is subjected to a long period of carbonization at moderate temperatures to form metallurgical coke.
demineralization – removal of mineral matter (ash) from coal by solvent extraction, usually under hydrogen atmosphere.
demonstration plant – a plant whose design is based on data derived from pilot-scale testing of sufficient capacity to demonstrate the large-scale feasibility of a process.
depolymerization – the change of a large molecule (e.g., coal polymers) into simpler molecules (e.g., aromatics, BTX), usually accompanied by the substitution of hydrogen for oxygen.
destructive distillation – the distillation of coal or other solids accompanied by their decomposition; destructive distillation of coal yields coke, tar, ammonia, gas, etc.
desulfurization – the removal of sulfur from hydrocarbonaceous substances by chemical reactions. Various processes are Claus, Appleby-Frodingham, C.S.I.R.O., ferric chloride leaching, Kennecott.
devolatilization – the removal of a proportion of the volatile matter from medium- and high-volatile coals to prevent subsequent caking.
dissolution – the taking up of a substance by a liquid with the formation of a homogeneous solution.
distillation – a process of evaporation and recondensation used for separating liquids into various fractions according to their boiling points or boiling ranges.
dolomite – a mineral having the chemical formula $CaMg(CO_3)_2$, i.e., a carbonate of calcium and magnesium.

ebullated bed – a boiling bed; gas, containing a relatively small proportion of suspended solids, bubbles through a higher-density fluidized phase, with the result that the system resembles a boiling liquid.
economizer – a heat exchanger for recovering heat from flue gases and using it to heat feedwater or combustion air.
effluent gas – gas issuing from a gasifier or combustor.
electrode carbon – see anode carbon.
elutriation – the preferential removal of the small constituents of a mixture of solid particles by a stream of high-velocity gas.
endothermic – a process in which heat is absorbed.
enthalpy – a form of thermal energy defined as the sum of the internal energy of a system plus the product of the system's volume and pressure.
entrained bed – a bed in which solid particles are suspended in a moving fluid and are progressively carried over in the effluent stream.
entrained flow – see entrained bed.
eutectic – that combination of two or more components which produces the lowest melting temperature.
exothermic – a process in which heat is liberated.
extraction – a process for dissolving certain constituents of a mixture by means of a liquid with solvent properties for selected components only.
extraction-hydrogenation – extraction carried out in the presence of hydrogen either as a gas or derived by transfer from hydrogen donor solvents.
extractive coking – similar to delayed coking process, with the emphasis on high tar yields to produce liquids.

filter cake – the moist residue remaining from the filtration of a slurry to produce a clean filtrate.
filtrate – a liquid free of solid matter after having passed through a filter.
filtration – the separation of solids from liquids by passing the mixture through a suitable medium, e.g., cloth, paper, diatomite.
Fischer assay – an assay for the determination of oil (tar) yields from coal or oil shale; conducted in a retort under an inert atmosphere with a gradual increase in temperature.
Fischer-Tropsch catalyst – iron and cobalt catalysts developed by Fischer and Tropsch for the catalytic synthesis of liquid fuels from coal-derived synthesis gas.
fixed bed – solid particles in intimate contact with fluid passing through them, but too slowly to cause fluidization.
fixed carbon – theoretically, the carbon content of coal which exists in the elemental state; practically, the difference between 100 percent and the sum of ash, moisture, and volatile matter percentages.
flash carbonization – a carbonization process characterized by very short residence times of coal in the reactor to optimize tar yields; also called flash pyrolysis.
flue gas – gas issuing from a combustor; either exhausted to atmosphere or expanded through a gas turbine.
fluidization (dense phase) – the turbulent motion of solid particles in a fluid stream; the particles are close enough to interact and give the appearance of a boiling liquid.
fluidization (entrained) – solid particles transported by a high-velocity fluid stream with little or no solid interaction.
fluidized bed – a bed through which a fluid is passed with a velocity high enough for the solid particles to separate and become freely supported in the fluid.
fly-ash – a fine ash from the pulverized coal burned in power station boilers, or entrained ash carried over from a gasifier.
fractionation – distillation process for the separation of the various components of liquid mixtures; an effective separation can only be achieved by the use of fractionating columns attached to the still; also called fractional distillation.
fuel cell – a galvanic cell in which the oxidation of a fuel (e.g., coal) is utilized to produce electricity.
fuel gas – low heating value product generally utilized on-site for power generation or industrial use.

gasification of coal – the conversion of solid coal into a gaseous form by any of a variety of chemical processes.
gasifier – a vessel in which gasification occurs, usually utilizing fixed-bed, fluidized-bed, or entrained-bed units.

high-Btu gas – a gas, largely methane, having a heating value of 900 to 1,000 Btu per cubic foot, which approaches the value for natural gas.
high heating value (HHV) – the heat liberated during a combustion process in which the product water vapor is condensed to a liquid.
hydrocoking – coking of tars, SRC, etc., under hydrogenating conditions to form liquid products.
hydrocracking – the combination of cracking and hydrogenation of organic compounds.

hydrogasification – gasification that involves the addition of hydrogen to the products of primary gasification to optimize formation of methane.

hydrogenation – chemical reactions involving the addition of hydrogen, present as a gas, to a substance in the presence of a catalyst under high temperatures and pressures.

hydrogen donor solvent – solvent, such as anthracene oil, tetralin (tetrahydronaphthalene), decalin, etc., which transfers hydrogen to coal constituents causing depolymerization and consequent evolution of liquid products of lower boiling range which are taken up by the solvent.

hydrotreating – a process involving the reaction of hydrogen with hydrocarbon mixtures for the removal of such impurities as oxygen, nitrogen, and sulfur.

ignition temperature – the minimum temperature necessary to initiate self-sustained combustion of a substance.

industrial gas – see fuel gas.

inerts – macerals in coal not readily changed by the action of solvents in the solvent extraction of coal, e.g., fusinite.

in situ – in its original place, e.g., underground gasification of a coal seam.

intermediate-Btu (IBtu) gas – synthesis gas product with an HHV between 250 and 500 Btu per standard cubic foot, consisting mainly of carbon monoxide and hydrogen.

kerogen – organic material from which shale oil is extracted.

lignite – a low rank of coal between peat and subbituminous.

limestone – a sedimentary rock composed mostly of calcium carbonate ($CaCO_3$) and possibly some magnesium carbonate ($MgCO_3$).

liquefaction – conversion of a solid to a liquid; with coal this invariably involves hydrogenation to depolymerize the coal molecules to simpler molecules.

liquified petroleum gas (LPG) – those hydrocarbons that have a vapor pressure (at 70°F) slightly above atmospheric (such as propane and butane); kept in liquid form under a pressure higher than 1 atm.

lock hopper – a mechanical device that permits the introduction of a solid into an environment of different pressure.

low-Btu (LBtu) gas – a gas having a heating value of 150 to 350 Btu per cubic foot; when made from coal, water, and air, it contains varying quantities of carbon monoxide, carbon dioxide, nitrogen, hydrogen, and methane.

moisture and ash-free (MAF) – a term that relates to the organic fraction in coal; "moisture- and mineral-matter free" is equivalent.

methanation – the production of methane (CH_4) from a mixture of carbon monoxide and hydrogen.

micron – a unit of length equal to 1 millionth of a meter.

natural gas – naturally occurring gas extracted from sedimentary structures consisting mainly of methane and having an HHV to 1050 Btu per standard cubic foot.

noncoking – a coal that does not form coke under normal coking conditions.

olefinic hydrocarbon – a class of unsaturated hydrocarbons containing one or more double bonds and having the general chemical formula C_nH_{2n}.

open cycle – a thermodynamic power cycle in which the working fluid passes through the system only once and is then exhausted to the atmosphere.

perfect gas – see ideal gas.

petrochemicals – those derived from crude oil or natural gas, or their coal-derived substitutes; they include light hydrocarbons such as butylene, ethylene, and propylene–the raw materials for the production of plastics by polymerization.

phenols – a group of aromatic compounds having the hydroxyl group directly attached to the benzene ring. They give the reactions of alcohols, forming esters, ethers, and thiocompounds; phenols are more reactive than the benzene hydrocarbons; derived from coal tar.

pilot plant – a chemical process plant containing all the processes of a commercial unit, but on a smaller scale, for the purpose of studying the process.

pipeline gas – a methane-rich gas that conforms to certain standards and having an HHV between 950 and 1,050 Btu per standard cubic foot. Standards include minimum water content, minimum inert gases, minimum hydrogen and carbon monoxide content, and its compressibility to 1,000 psig.

process development unit – a laboratory-sized system used to study the effects of process variables on performance.

proximate analysis – analysis of coal based on the percentages of moisture, volatile matter, fixed carbon, and ash.

purification – removal of the wide range of impurities present in gases from coal gasification to yield purity gas. See Rectisol process.

pyrolysis – thermal decomposition of organic compounds in the absence of oxygen.

quenching – cooling by immersion in oil or water bath or spray.

Raney nickel catalyst – nickel sponge used as a catalyst in the hydrogenation of organic materials and the methanation of synthesis gas to methane.

raw gas – see crude gas

reactivity – susceptibility to chemical change; in coal conversion, the reactivity of the coal for conversion to liquid products is a function of the MAF volatile matter content and the petrographic composition of the coal.

reactor – vessel in which coal-conversion reactions take place.

reducing gas – used as a reducing agent in redox reactions, e.g., hydrogen, superheated steam.

reforming processes – a group of proprietary processes in which low-grade or low molecular weight hydrocarbons are catalytically reformed to higher grade or higher molecular weight materials; also applies to the endothermic reforming of methane, for the production of hydrogen by the reaction of methane and steam in the presence of nickel catalysts.

refractory – a material capable of withstanding extremely high temperatures and having relatively low thermal conductivities.

residence time – time spent by a typical particle in a reaction zone.

retort – distill or decompose by heat.

saturated hydrocarbon – a hydrocarbon in which all bonds are single covalent bonds and none are double or triple bonds.

scrubber – apparatus in which a gas stream is freed of tar, ammonia, and hydrogen sulfide.

semi-water gas – a mixture of carbon monoxide, carbon dioxide, hydrogen, and nitrogen obtained by passing an air-stream mixture through an incandescent bed of coke; HHV about 120 Btu per standard cubic foot.

sensible heat – that heat which results in only the elevation of the temperature of a substance with no phase changes.

shift conversion – process for the production of gas with a desired carbon monoxide content from crude gases derived from coal gasification; carbon monoxide rich gas is saturated with steam and passed through a catalytic reactor where the carbon monoxide reacts with steam to produce hydrogen and carbon dioxide, the latter being subsequently removed in a wash plant. The ratio of hydrogen to carbon monoxide in the product gas can be changed at will.

sintering – the agglomeration of solids at temperatures below their melting point, usually as a consequence of heat and pressure.

slag – a molten mixture of various metallic oxides and salts.

slurry – a suspension of pulverized solid in a liquid.

solvation – the association or combination of molecules of solvent with solute ions or molecules.

solvent – that component of a solution which is present in excess, or whose physical state is the same as that of the solution.

solvent extraction – selective transfer of desired coal constituents from finely divided coal particles into a suitable solvent after intimate mixing, usually at high temperatures and pressures in the presence of hydrogen, with or without a catalyst, followed by phase separation.

solvent refined coal (SRC) – a coal extract derived by solvent extraction; a brittle, vitreous solid (M.P. 300°F to 400°F) containing about 0.1 percent ash and about 10 percent of the sulfur in the original coal feedstock; calorific value is about 16,000 Btu per pound. May be used as a clean fuel for power generation by combustion; utilized for the production of high-grade metallurgical coke, anode carbon, and activated carbon by coking; or hydrogenated to produce synthetic crude oil.

space velocity – the volume of a fluid (usually measured at standard conditions) passing through a unit volume in a unit time; units are in reciprocal time.

spectroscopic – spectral or pertaining to the optic spectrum.

standard cubic foot (scf) – the volume of a gas at standard conditions of temperature and pressure. The American Gas Association uses moisture-free gas at 60°F and 30 inches of mercury (1.0037 atm) as its standard conditions. The pressure standard is not universal in the gas industry; 14.7 psia (1.000 atm) and 14.4 psia (0.980 atm) are also used. The scientific community uses 32°F and 1 atm as standard conditions.

stoichiometry -- the definite proportions in which molecules react chemically to form new molecules.

stripping – the removal of the more volatile components from a liquid mixture of compounds.

subbituminous coal – the rank of coal between bituminous and lignite, classified by ASTM as having a range of heating values between 8,300 and 11,000 Btu per pound on a moist mineral-matter-free basis.

substitute natural gas (SNG) – a synthetic gas conforming to natural gas standards.

superficial velocity – the linear velocity of a fluid flowing through a bed of solid particles calculated as though the particles were not present.

superheater – a heat exchanger which adds heat to the saturated steam leaving a boiler.

syncrude – synthetic crude oil; oil, produced by the hydrogenation of coal or coal extracts, which is similar to petroleum crude.

synthesis gas – a mixture of hydrogen and carbon monoxide which can be reacted to synthesize a hydrocarbon.

tail gas – a gas issuing from a gas-treatment unit which may be recycled to the process or exhausted.

tar (coal) – a dark brown or black, viscous, combustible liquid formed by the destructive distillation of coal.

therm – a unit of heat used as a basis for the sale of natural gas; equal to 100,000 Btu.

thermal recovery (TR) – a petroleum recovery process that utilizes heat to thin viscous oil in an underground formation and allows it to flow more readily toward wells through which it can be brought to the surface.

topping cycle – the higher temperature thermodynamic power cycle of a combined-cycle system.

turned down -- the reduction of reactor flow rates to a fluidized-bed reaction vessel.

ultimate analysis – the analysis of coal based on the percentages of chemical elements.

volatile matter – those constituents of coal, exclusive of moisture, that are liberated from a sample when heated to 1,750°F (for 7 minutes) in the absence of oxygen.

water gas – gas produced by the reaction of carbon and steam to provide mixtures of carbon monoxide and hydrogen; similar to synthesis gas.

water gas shift – the reaction between water vapor and carbon monoxide to produce hydrogen and carbon dioxide or the reverse: $CO + H_2O \rightleftarrows H_2 + CO_2$.

working fluid – a gas stream which directly does work, e.g., powering a gas turbine.

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