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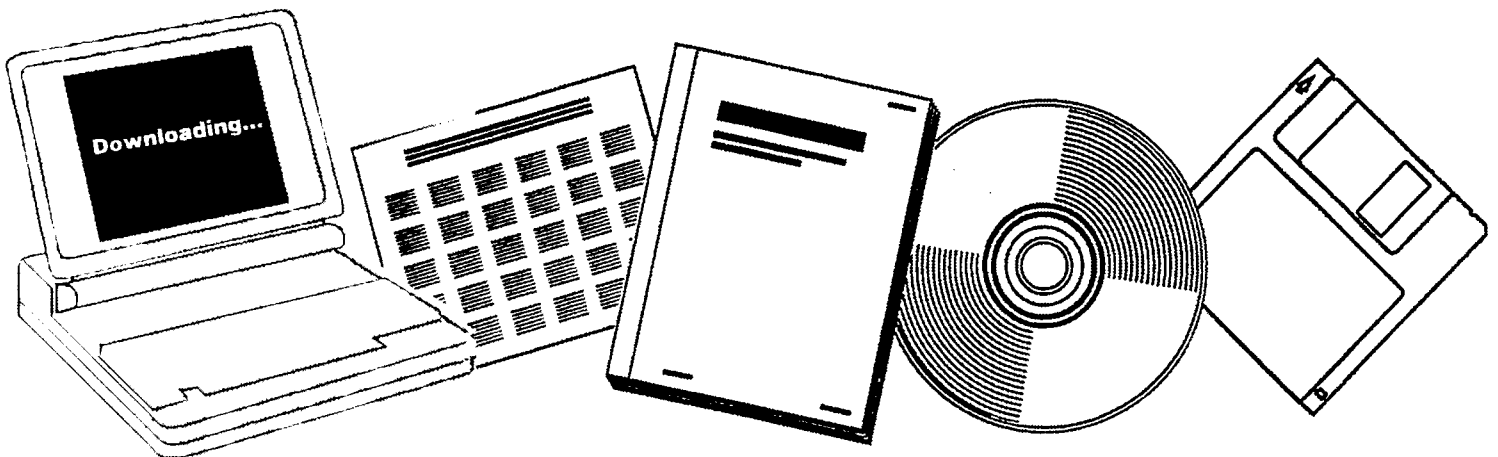
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# SUPPORTING RESEARCH AND DEVELOPMENT FOR COAL PROGRAMS

USAEC, WASHINGTON, D.C

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## SUPPORTING RESEARCH AND DEVELOPMENT FOR COAL PROGRAMS

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**MASTER**

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## VI. SUPPORTING RESEARCH AND DEVELOPMENT

SUMMARY

The supporting or applied research and development effort within the Coal Program, as distinguished from the basic or multidirectional research, has the objective of providing essential research support required to ensure the technological success of the coal conversion options as currently identified. The basic research contributions, on the other hand, address the more fundamental problems which are expected to lead to an understanding of the underlying principles of the phenomena encountered. New concepts for new processes, improvements for present processes, and improved materials are expected to result from applied research efforts as well as the basic. Correlation of these efforts should be emphasized to maximize such benefits.

The supporting or applied research effort for coal conversion is characterized by the recommended FY 1975 funding base for the following five subdivisions (the basic research program is discussed under Molecular Sciences and Materials Sciences categories in the Division of Physical Research chapters).

	<u>FY 1975</u> <u>(\$ millions)</u>
Chemical development	9.4
Engineering science support	5.0
Materials	13.5
Systems evaluation	0.8
Geoscience	<u>0.2</u>
Total	28.9

The funding level of \$28.9 corresponds to the cumulative FY 75 estimate support currently distributed among the Federal agencies which would likely be transferred into ERDA. It amounts to about a six percent incremental addition to the coal technology program and is recommended only as a base on which an expanded and sustained supporting research and develop-

ment program should be built. This level should, therefore, be considered to be a minimum recommended level in view of the deficiency inherited as a result of underfunding this activity in the past. The distribution within the five subcategories shown above represents our present judgment of relative needs within the Supporting Research and Development category. However, the level of effort required to adequately scope a detailed supporting research program far exceeds the available manpower for this contingency task force. In that regard, this chapter is deficient.

It is recommended that the Director of the Coal Programs Division establish an on-going supporting research program at the national laboratories and energy research centers. It is also recommended that a review of research needs be made to guide the formation of the supporting research program and to develop the resources of national laboratories and energy centers.

#### INTRODUCTION

The large and rapidly developing fossil fuels industry - including mining, coal liquefaction, coal gasification, newer combustion methods, shale oil mining, and conversion - must have a solid supporting R/D base (as well as the basic research effort described in DPR's chapter) for several urgent reasons: (1) Percentagewise, small process improvements, such as increased yields or diminished corrosion rates due to materials improvements, would as a consequence of the industry size have significant economic impact; (2) The supporting research and development effort provides the information needed for development of new and improved processes. Because of the long lead times involved in large industrial projects, it is essential to initiate a strong R&D effort as early as

possible in order to maximize its effect on the rapidly growing industry;

(3) The separate conversion processes often have unrecognized common problems which can be related through the support program and answered with a common solution. This on-going effort cannot only find solutions for known problems, but also anticipate new problem areas before they occur. This foreknowledge can be used to guide the projects and avoid program delays;

(4) Recently there have developed constraints on industrial expansion which have heretofore played a less prominent role, and hence intrude into areas where there exists an insufficient fund of information. These areas include employee health and safety, environmental effects of industrial activity, and potential raw materials scarcities.

#### OBJECTIVES

- (1) Provide the Coal Program with broad research support capable of addressing in an appropriate time frame problems important to the development of coal conversion processes and methods of coal utilization.
- (2) Provide a source of new concepts leading toward improved processes, higher efficiencies, and superior materials.
- (3) Make available to the developing coal industry an adequate supply of well-trained personnel well-versed in modern scientific and engineering techniques.

It is a judgment of the planning group that these objectives may reasonably be carried out with a budget level of approximately 9 to 15% of the total program.

SCOPE

The applied research and development work covered in this section is directed toward providing the essential support for the coal program. In this sense, the work may be thought of as "applied" since the problems to be dealt with bear upon those which may be expected to arise in activities relating to coal processing and coal utilization. However, the skills and techniques involved could be indistinguishable from those called for in less mission-oriented research.

The problems dealt with in this Supporting Research and Development section differ from those treated within the specific topical areas of Mining, Improved Combustion Systems, Synthetic Fuels, Environmental Controls Technology in the respect that the work has a somewhat broader supportive scope, and is generally restricted to smaller scale laboratory or bench-scale efforts. Thus, larger scale tasks, clearly applicable to one of the named subject categories within the coal program, will be carried out within the purview of that branch.

A detailed applied R/D program cannot be formulated with the limited manpower available for this portion of the contingency study. Only broad areas of need can be listed. Remedial action for this deficiency is recommended at the end of the chapter.

PRESENT PROGRAMS IN THE AREA OF SUPPORTING RESEARCH  
AND DEVELOPMENT FOR COAL

Funding in this area is presently (i.e., pre-ERDA) provided for in the Office of Coal Research, Bureau of Mines, AEC, EPA, and National Science Foundation budgets. In some cases the budget levels shown are approximations obtained from preliminary information or from incomplete descriptive material. Direct coordination with the agencies is required to reduce the uncertainties in these estimates.

Particularly speculative at this time is the appropriate portion of the EPA Environmental Controls Technology Program which should logically be transferred into the Supporting R/D area. The elements of this program are listed in Table 6.1 showing an estimated total for FY 1975 of  $\$19.3 \times 10^6$ . Some presently nonestimable fraction of this effort may be characterized as Supporting R/D. However, it is believed to be rather small (less than 5%) and so will be neglected at this time.

The estimated total available funds for FY 1975 in the area of Supporting Research and Development for Coal is shown in Table 6.2 to be  $\$28.9 \times 10^6$  exclusive of EPA funds. This table lists for each of the six budget categories from which Supporting R/D monies are drawn the estimated division of funds between supporting and basic research, and the relationships to the total Coal Program within each category.



Table 6.1. Elements of the EPA Environmental Controls Development Technology Program Related to Coal<sup>a</sup>

	FY 1975 (millions)
Mining	<u>3.7</u>
Eastern Underground	
Eastern Surface	
Western	
Direct Combustion	<u>13.1</u>
NO <sub>x</sub> Control	
Fluidized Bed	
Synthetic Fuels	<u>6.9</u>
High Btu Gasification	
Coal Liquefaction	
Low Btu Gasification	
Common Technology-Environmental Control	<u>55.6</u>
Flue Gas Desulfurization	30.9
Fuel Cleaning	9.7
Particulate Control	
Conversion Process Control	
Waste Disposal/By-Product Utilization	
Thermal Pollution Control	
Noise	
Intermedia Effects	
Total	<u>79.3</u>

<sup>a</sup>EPA proposed program for FY 1975.

Table 6.2. Coal Research and Development Budget Estimates  
 FY 1975 Congressional Budget  
 (Millions of Dollars)

	Total	Total Coal Program	Coal-Related Research		
			Applied	Basic <sup>a</sup>	Total
AEC-DPR <sup>b</sup>	80.7	1.7	0	1.7	1.7
Materials Sciences	40.6	0.5	0	0.5	0.5
Molecular Sciences	40.1	1.2	0	1.2 <sup>c</sup>	1.2
AEC-DAT <sup>b</sup>	24.4	4.5	1.0	0	1.0
DOI-USBM <sup>c</sup>		105.6	9.9	5.7	15.6
DOI-OCR <sup>c</sup>		283.4	15.3	3.8	19.1
NSF-RANN <sup>d</sup>	148.9		2.7	1.1	3.8 <sup>e</sup>
NSF-RES <sup>d</sup>	363.7	8.7	0	8.7	8.7
Chemistry	37.1	6.3	0	6.3	6.3
Materials Research	45.4	2.4	0	2.4	2.4
Total			28.9	21.0 <sup>a</sup>	49.9

<sup>a</sup>Multidirectional in character - may apply to programs other than coal.

<sup>b</sup>AEC Congressional Budget, January 1974.

<sup>c</sup>DOI. "Energy Research Program of the USDOJ," February 1974.

<sup>d</sup>NSF FY 1975 Budget to the Congress, January 1975.

<sup>e</sup>\$2.7M of 3.8 is energy add-on.

Regarding Table 6.2 we note that all DPR funds are essentially basic or multidirectional in character. Applied problems are frequently addressed from a basic or fundamental point of view using the existing base of expertise developed within these basic research programs. Materials science funds for coal-related corrosion research are estimated to be \$0.5M.

The DAT funds support both developmental and supportive research efforts. It is estimated that approximately \$1.0M of the \$4.5M total is supporting research. Little basic research effort is judged to be supported with these funds.

The NSF-RANN coal research program totals \$3.8M. The split between supporting and basic research is difficult to judge; the basic portion could be 30% or more. Interaction with NSF-RANN, however, is required to establish this split.

The NSF-Res. coal research for materials is not possible to estimate with reasonable accuracy without more information. The total NSF-Materials effort which is identified as energy-related is \$11.8M (\$45.4 total). Only a fraction of this could be reasonably construed to be coal related - perhaps as much as 20%. The chemistry effort identified as energy-related is \$23.4M (\$37.1M total). An estimated \$6.3M is coal-related and all characterized as basic research.

The DOI-USEM coal effort in High-Btu gas is virtually all applied or developmental research - except for a fraction of the work under Hydrogen Generation. The Support Research under Coal Liquefaction (\$7.1M) and the Advanced Hydrocarbons Research (\$3.2M) appear to be about 50% basic with the rest applied.

Central Station Conversion on Advanced Cycles and Direct Combustion is \$3.3M and is judged to be 10% applied research or \$0.3M.

The Central Station Conversion on Coal Combustion is funded at \$2.0M and is judged to be 10% or \$0.2M.

The DOI-OCR Advanced Research Supporting Technology is given as \$19.1M. Of this, approximately 20% is construed to be basic in character, viz \$3.8M. Greater accuracy here requires direct communication with OCR.

RECOMMENDED PROGRAM - SUPPORTING RESEARCH  
AND DEVELOPMENT FOR COAL

The Subpanel V report\* recommended the following subdivisions of work in this area:

- Equipment development
- Materials
- Data compilation, handbooks, analyses
- Catalysts and chemical kinetics for conversion processes
- Process development
- Hydrogen production for use in coal conversion processes

The last three items could logically be grouped as "Chemical Development." Hence, we now recommend the modified topical subdivisions listed in Table 6.4 which represents the recommended budget for the Applied Research and Development Program.

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\* The Nation's Energy Future, Subpanel V Report Coal and Shale Processing and Combustion, Oct. 27, 1973.

Table 6.3 Estimates of the Office of Coal Research Program<sup>1</sup>

	FY 75 (Millions)
<u>Supporting Science &amp; Technology</u> .....	<u>\$ 19.1</u>
Advanced Coal Conversion Process .....	12.5
Gasification	
Catalytic Methenation	
Liquefaction	
Improved H <sub>2</sub> Production	
Conversion of Gas to Liquid Fuels	
Advanced Utilization Processes .....	2.6
Extraction, Refining, Conveyances	
Clean Combustion	
Sulfur Removal Processes	
New & Improved Electric Power Generation .....	1.0
Improved Fuel Cells	
Combined Cycles	
Advanced Supporting Research .....	3.0
Materials	
Waste Disposal Processes	
Physical-Chemical Measurements	

<sup>1</sup>Information from Jere Nichols  
 Alex Mills, AD  
 Harold Podal - Chemistry (petroleum ind.), OSW  
 Henry Frankel - Materials, NASA

Table 6.4. Supporting Research and Development for Coal -  
Recommended Budget

	FY 1975 (millions)
<u>Supporting Research and Development</u>	
Chemical Development	9.4
Advanced conversion processes, catalyst development analysis and hydrogen production, structure and properties of coal, combustion processes, sulfur removal, hydrocarbon research	
Engineering Sciences	5.0
Process development, extraction, refining and conveyances, separation processes, combined cycles, waste disposal processes, size reduction	
Materials Research	13.5
Failure analysis, corrosion, erosion, compatibility testing, bonding	
Systems Evaluation	0.8
Process analysis, data availability and compilation	
Geosciences	0.2
Rock mechanics, fracture analysis	
Total	28.9

The scope of the tasks falling within "Supporting Research and Development" for the Coal Program are indicated in Table 6.4. Five general subdivisions are noted: Chemical Development, Engineering, Science Support, Materials, Systems Evaluation, and Geoscience. Suggested funding distribution between these areas are indicated reflecting present views of the relative needs. Also indicated are further task subdivisions in four of the five defined general areas as an illustration of the type of work to be undertaken within each category.

As indicated earlier, a detailed program layout can not be done with the resources available for this planning exercise. Lacking specificity, it is impossible to identify lists of problems which exist in the present coal program and lists of research programs to attack these problems. Since the problem - attack relationship can not be clearly illustrated, it is difficult to show a strong case for the justification of a supporting research program in this planning document.

Yet there is a dire need for sustained applied research in support of coal conversion technology. We attempt to show that this need exists by several means. First, there are appended two lists of supporting research projects which address current problems in coal conversion. These project lists originated in the national laboratories and are meant to be examples. They show a problem area and a plan of attack, and they present six million dollars of research in the first year.

As a second proof that supporting research is needed we can cite the success of the AEC weapons programs and the NASA Apollo project.

These were backed with vigorous sustained supporting research programs.

Finally, the growth of supporting research in the Office of Coal Research shows a recognition that such work is needed to implement coal process development. As recommended in this chapter, the applied coal research effort must grow faster.

#### MANAGEMENT COMMENTS AND RECOMMENDATIONS

The work performed in the area termed "Supporting Research and Development" within the Coal Program impinges on the direct programmatic work within each of the other co-equal activities of the Coal Program on the one hand, and with the more general basic research endeavors which span all programs - Fossil, Nuclear, Environmental Science - on the other. There is bound to be some overlap in each direction, and we view some overlap as desirable.

It is recommended that the Director of the Coal Programs Division should establish and maintain an on-going supporting coal research program at the national laboratories and energy field centers. As a first step, the Director should ask the field centers and laboratories to prepare an incremental package of supporting research proposals which could be initiated this fiscal year. This should be followed by a major team effort to review expected problem areas and to define the associated needed applied research. The results of the review should be reflected in the FY 76 program and budget. The resources of the national laboratories and energy field centers should be surveyed and, based on the defined applied research program, guidance should be offered to correct any deficiencies. Likewise, the resources of research and development laboratories in the private sector should be surveyed for use in the supporting coal research program.



The following lists of supporting research projects, appendices 6A and 6A, are meant only to be examples, as stated in the text. They do, however, exemplify the nature of sustained supporting research that ERDA must have.

APPENDIX 6A  
PROPERTIES AND REACTIONS OF COAL - I

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<b>CATALYSIS</b>							
<p>Catalysis plays a key role in most of the processes for conversion of coal to clean fuels, whether solid, liquid or gaseous. Even where a catalyst is not deliberately added, mineral matter in the coal may have a profound effect on the course and kinetics of reaction. Much empirical work has been and is being done on improvement of catalysts for coal processing; studies of catalysts and of the mechanisms of catalytic reactions may facilitate the selection of catalysts and optimization of reaction conditions.</p>							
<p><u>Identification of "Initial" Volatile Products of Catalytic Coal Reactions.</u> Use of the extreme sensitivity and selectivity of analytical systems based on time-of-flight mass spectrometry to identify the "initial" products of coal hydrogenation, and to evaluate the performance of a catalyst by detecting the onset of specific reactions. Elucidation of reaction mechanisms by isotopic labeling. Correlation of coal reactions with those of model compounds. Investigation of the role of metal carbonyls in coal conversion reactions.</p>							
	ANL	0.10	0.15	0.15	0.15	0.15	0.15
<p><u>Catalysis of Coal Reactions by Mineral Components.</u>  <u>Identification of minerals responsible for "ash" catalysis, particularly in solvent refining of coal, and study of mechanism of action.</u></p>							
	ANL	0.05	0.05	0.05	0.05	0.05	0.05

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>S,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<u>Structure and Extent of Simple Organic Molecules Within the Coal Lattice.</u> Use of time-of-flight mass spectrometry and gas chromatography to study the structure and extent of occurrence of relatively simple organic molecules within the coal lattice and conditions under which they can be released. Comparison of products released by heating with those obtained by low temperature solvent extraction.	ANL	0.10	0.10	0.10	0.10	0.10	0.10
<u>Physical and Chemical Properties of Coal.</u> Correlation of physical and chemical properties of coal with hydrogenation and gasification reactivities. Properties to be investigated include chemical composition, particle size distribution, porosity, surface area, surface features, X-ray structure, electron spin resonance, and thermal transitions.	BNL	0.10	0.10	0.10	0.10	0.10	0.10
<b>3. REACTIONS OF COAL</b>							
<u>Desulfurization of Coal by Gas-solid Reactions.</u> Studies of selective oxidation and reduction of sulfur in solid coal by oxygen and hydrogen gases, respectively.	Ames	0.07	0.10	0.10	0.10	0.10	0.10

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<u>Mechanisms of Dissolution of Coal.</u> Studies of the mechanisms of solvent extraction of coal using isotopically-labeled solvents and gases together with gas chromatography and mass spectrometry.	ANL	0.10	0.10	0.10	0.10	0.10	0.10
<u>Study of Fast, High-temperature Reactions of Coal With Hydrogen.</u> Kinetic studies in small-scale static and flow systems, using rapid heating techniques and detection of stable and free-radical products. Correlation of results with physical and chemical characteristics of the coal sample.	BNL	0.06	0.10	0.10	0.10	0.10	0.10
<u>Maximization of CO Production in Coal Combustion.</u> Kinetic studies of the reaction between carbon and oxygen diluted with CO <sub>2</sub> , to test the feasibility of simultaneous production of power and methanol in a combined cycle process.	BNL	0.07	0.10	0.10	0.10	0.10	0.10
<u>Reaction of Coal with Metal Oxides.</u> Investigation of the formation of metal carbides at readily attainable temperatures. Studies of the conversion of such carbides to gaseous and liquid fuels.	BNL	0.08	0.10	0.10	0.10	0.10	1.10
<u>Thermochemistry of Coal Reactions.</u> Thermodynamic calculations of coal conversion processes are generally based on data for carbon in the form of beta-graphite. More reliable results would be obtained if measurements were available for various types of coal.	ORNL	0.10	0.10	0.10	0.10	0.10	0.10

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<b>MECHANICAL PROCESSES</b>							
<p><u>Solid Particle Erosion of Vessel Walls.</u> Severe erosion-corrosion conditions exist in gasifier reactor and heat recovery systems, involving both ductile and brittle materials. On a ductile surface, the kinetic energy of the particle is dissipated in plastic work, which causes indentation or shearing of the surface. On a brittle surface, the kinetic energy is dissipated in crack propagation, which causes spalling of the surface. In these systems, the presence of corrosive gases complicates the erosion problem. The investigation will, therefore, involve the study of the mechanism of solid particle erosion at high temperature and pressure, where corrosion plays an important role.</p>	ANL	0.2	0.2	0.25	0.25	0.25	0.25
	Bu Mines	0.1	0.1	0.1	0.1	0.1	0.1
	Univ.	0.1	0.1	0.1	0.1	0.1	0.1
<p><u>Feeding and Removal of Solids at High Pressure.</u> The feeding and removal of coal at high pressure can cause severe erosion and abrasion problems. Lock hoppers have been used, however, there is an energy loss associated with them. Large pistons that displace coal into the pressure vessels have been tested. Also, coal has been pumped as a slurry with oil or water into the vessels. This, however, can create a separation problem for the recycling of the slurry fluid. In all of these systems erosion and abrasion of components occur. Research is needed into understanding the mechanical interactions so that present devices may be improved and new devices may be developed. This program will be coupled closely with the metallurgical programs on erosion and wear.</p>	ANL	0.05	0.05	0.05	0.05	0.05	0.05
	Bu Mines	0.15	0.15	0.15	0.15	0.10	0.10

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<p><u>Fundamental Study of Abrasive Wear.</u> Abrasive wear is a problem throughout the coal/slag/char/ash system in any coal process, from crushing and sizing of coal to the handling of ash and waste products. Abrasive wear is the removal of material from the surface by mechanical action, and may have normal as well as tangential components. The mechanism of abrasive wear relating to such phenomena as gouging abrasion and high stress grinding requires fundamental study. The case of low stress scratching abrasion will be covered under solid particle erosion studies.</p>	ANL	0.05	0.05	0.1	0.1	0.1	0.1
	Univ.	0.05	0.05	0.05	0.05	0.05	0.05
<p><u>Coal Size-reduction Processes and Particle Character.</u> A fundamental understanding of coal crushing and grinding is not available today. Large fractions of undersized particles are still produced in the grinding step. These particles do not react efficiently in many coal conversion processes, either due to their size or to their surface character. This study will investigate existing and new reduction techniques and the size and character of the resultant particles. This study will also rely heavily on data collected on the physical properties of coal.</p>	LBL						
	PNI	0.05	0.05	0.05	0.05	0.05	0.05
	DNL	0.1	0.1	0.15	0.15	0.15	0.1
	Univ.	0.05	0.05	0.05	0.05	--	--
	Bu Mines	0.1	0.1	0.15	0.15	0.2	0.15

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<p><u>High Temperature NDT Analysis of Vessel Walls.</u> Layered structures (e.g., ceramic linings on metal), thick-walled stainless steel vessels, or welds containing slag will require new test approaches for nondestructive testing of component performance during plant operation. Acoustic emission, ultrasonic analysis, and other new methods will be employed to demonstrate their validity at the high operating temperature. The testing method and instrument description will be incorporated into the ASME Boiler and Pressure Vessel Code to allow certified reliability.</p>	ANL	0.1	0.1	0.15	0.15	0.1	0.1
<p><u>Fluid Dynamics in 3-phase Packed-bed Systems.</u> The conversion of coal to liquids at high temperature and pressure occurs in packed beds of catalyst under hydrogen. Little information, other than empirical is available on the fluid dynamics of the 3-phase system. Information is needed on mass transfer rates between coal, liquid, and catalyst, pressure drop per unit of reactor length, and effects of scaleup in reactor diameter on these properties. Fundamental knowledge is needed on fluid and solid-phase properties. Information is also needed on proper liquid and gas ratios for adequate turbulence to avoid caking and coating of catalyst pellets. This program will investigate the basic fluid dynamics of the system of a fixed bed and slurry-gas mixture to obtain the needed correlations.</p>	ANL Ind. Univ.	0.1 0.05 0.05	0.1 0.05 0.05	0.1 0.05 0.05	0.1 0.05 0.05	0.1 0.05 0.05	0.1 0.05 0.05

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<b>SURFACE REACTIONS</b>							
<u>Fundamentals of Contact Between Solids and Fluids.</u>							
Coal conversion processes employ fluidized, entrained, and fixed-bed reaction vessels operating at high temperatures and pressures. However, the fundamental physical and chemical reactions at particle interfaces in coal systems are not clearly understood. These include thermodynamic activity, porosity, surface area and energy, and fluid and solid mass-transfer rates. A basic investigation will be undertaken to evaluate these mechanisms as a function of fluid and solid composition, temperature, pressure, and time. The investigation will also be coupled closely with the study on catalytic activity.	ANL PNL	0.2 0.1	0.2 0.1	0.2 0.1	0.2 0.1	0.2 0.1	0.2 0.1
<u>Failure Mechanisms in Vessels.</u> Ceramic liners, metal vessels, and structural components of coal conversion equipment are subject to thermal shock and fatigue during operation. The mechanism of ductile and brittle fracture under such stress state can be totally different than under steady-state conditions. The presence of a corrosive environment may lower the failure threshold or change the failure mechanism. This study will focus on thermal and environmental effects on the threshold values for brittle or ductile fracture.							
	ANL BNL In <sup>2</sup>	0.05 0.15 0.05	0.05 0.15 0.05	0.05 0.15 0.05	0.05 0.15 0.05	0.05 0.15 0.05	0.05 0.15 0.05



PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>\$,M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<b>CERAMICS</b>							
<p><u>Bonding of Ceramics to Metal Substrates.</u> Ceramic linings in coal conversion systems offer significant advantages of thermal insulation coupled with high chemical stability and wear or erosion resistance at elevated temperatures. A promising method that allows the tailoring of ceramic coatings in terms of their composition, microstructure and density is the plasma spray process. The purpose of this investigation is to gain an understanding of the relationship between the plasma deposition parameters (ceramic/substrate composition, rate and distance of deposition, temperature of substrate, etc.) on the resultant microstructure, bond strength and thermal shock resistance of the coatings. Attention will be focused on ceramic/metal combinations suitable for coal conversion atmospheres. Duplex structures consisting of low density ceramic insulators covered by wear resistance high density ceramic coatings will also be investigated.</p>							
	ANL	0.15	0.15	0.15	0.10	0.10	0.10
	Univ.	0.05	0.05	0.05	0.05	0.05	0.05
	Bu Mines	0.05	0.05	0.05	0.1	0.1	0.05

PROPERTIES AND REACTIONS OF COAL (Contd.)

<u>Topic</u>	<u>Lab</u>	<u>S, M-FY75</u>	<u>76</u>	<u>77</u>	<u>78</u>	<u>79</u>	<u>80</u>
<b>HY-PRODUCT RECOVERY</b>							
<u>Removal and Recovery of Sulfur at High Temperature.</u> In today's coal gasification processes, sulfur, as H <sub>2</sub> S, is recovered by commercial low-temperature methods (Alkazid, Benfield, rectisol, selexol, sulfinol, etc.). Efficiency is reduced since the gas stream originally at as high as 1000°C temperature must be quenched to 100-150°C. Existing methods for high temperature desulfurization have serious limitations. These existing processes must be improved and new methods must be conceived and developed. Promising techniques will be evaluated at operating gasifiers.	Ames	0.2	0.2	0.2	0.2	0.15	0.1
	Bu Mines	0.1	0.1	0.15	0.2	0.2	0.15
<u>Mineral Recovery from Coal Waste Products.</u> Analyses of ash from eastern and western coal show that they contain oxides of the following elements: silicon (30-60%), aluminum (20-30%), iron (5-20%), calcium (2-12%), sulfur (1-12%), and traces of others. Presently, ash is used as source material for cement and aggregate manufacture. However, when large quantities of coal are utilized, consideration must be given to recovery of their minerals. Of these, aluminum oxide recovery appears to be attractive for aluminum manufacture. The objective of this study would be to evaluate these possibilities in consultation with coal processors so that recovery can be optimized.	Univ.	0.05	0.05	0.05	0.05	0.05	0.05
	Ind.	0.05	0.05	0.1	0.1	0.1	0.1

APPENDIX 6B

PROPERTIES AND REACTIONS OF COAL - II

ORNL

1.	COMPOSITION OF COAL . . . . .	<u>\$300,000</u>
1.1	Constitution and Structure of Coal Microconstituents ..	\$180,000
1.2	Identification of Trace Metal Complexes in Coal .....	120,000
2.	CHEMISTRY OF COAL CONVERSION . . . . .	<u>\$720,000</u>
2.1	Heteroatom Removal From Coal by Catalytic Hydrogenolysis .....	\$120,000
2.2	Hydrocracking, Hydrogen Addition, and Condensation Reactions in Coal Liquefaction .....	120,000
3,1 <sup>o</sup>	2.3 Thermodynamic Data for High Temperature Coal Processing .....	120,000
2.4	The Thermodynamics of Coal-Related Hydrocarbon in Solutions at High Temperature .....	120,000
2.5	Modeling of Rearrangements of Coal Precursors and Coal Liquefaction Products .....	120,000
2.6	Fundamental Hydrogenation and Rearrangement Reactions Related to Coal Chemistry by the use of Nuclear Magnetic Resonance Spectroscopy .....	120,000
3.	ANALYTICAL CHEMISTRY . . . . .	<u>\$250,000</u>
3.1	Chemical Characterization of Materials Used and Produced by Coal Hydrogenation Technology .....	\$ 90,000
3.2	Development of Multi-Component Analytical Techniques for Coal-Related Materials .....	90,000
3.3	Development of Specialized Analytical Instrumentation for Coal Hydrogenation Research .....	70,000
4.	SEPARATIONS SCIENCE . . . . .	<u>\$655,000</u>
4.1	Activated Carbon Studies .....	\$120,000
4.2	Multiphase Flow in Porous Bodies .....	75,000
4.3	Engineering Sciences .....	90,000
4.4	Biological Processing of Coal .....	120,000
4.5	Filtration Research .....	100,000
4.6	Effluents from Coal Liquefaction .....	150,000

PROPERTIES AND REACTIONS OF COAL (Cont.)

5. CATALYSIS . . . . .	<u>\$600,000</u>
5.1 The Selection and Improvement of Catalysis Related to Coal Conversion Process Development . . . . .	\$ 60,000
5.2 Solid State Aspects of Heterogeneous Catalysis Related to Coal Research . . . . .	120,000
5.3 Mechanisms of Interaction Between Coal and Molten Salt Hydrocracking Catalysts . . . . .	180,000
5.4 Molten Salts in Coal Utilization . . . . .	120,000
5.5 Catalytic and Surface Studies . . . . .	120,000
6. MATERIALS RESEARCH FOR COAL CONVERSION PROCESSES	<u>\$720,000</u>
6.1 Solid Particle Erosion of Metals and Ceramics . . . . .	\$120,000
6.2 Behavior of Metals and Ceramics in Coal Treatment Systems . . . . .	120,000
6.3 Hydrogen Embrittlement . . . . .	120,000
6.4 Failure Mechanisms in Reaction Vessels . . . . .	120,000
6.5 Mass Transport in Ceramics . . . . .	120,000
6.6 Deformation and Fracture of Ceramics . . . . .	120,000

## PROPERTIES AND REACTIONS OF COAL

### 1. COMPOSITION OF COAL

#### 1.1 Constitution and Structure of Coal Microconstituents # MY - 3 \$180,000

This project is a study of the constitution and structure of coal microconstituents (macerals and minerals) by such nondestructive physical methods as x-ray diffraction and fluorescence; electron microscopy, diffraction, and spectroscopy (ESCA); and optical absorption, reflection, and fluorescence spectroscopy (UV, VIS, and IR). Emphasis will be placed on techniques and problem areas in which OPNL has special expertise. An existing coal petrography laboratory and a service facility for the separation and physical fractionation of coal microconstituents will be integral parts of the program. Constituents of coal of various botanic origins and with various metamorphic histories will be studied and compared. Topics of initial study will include low- and high-angle x-ray diffraction studies of intermolecular and macromolecular spatial ordering, x-ray fluorescence and ESCA studies of the distribution of minor and trace elements, and electron microscopic studies of maceral textures and their ultrafine pores. The results of these studies should contribute to a better understanding of the geologic evolution of coal and should provide a firmer basis for evaluating the characteristics and properties of these complex materials for purposes of utilization.

#### 1.2 Identification of Trace Metal Complexes in Coal # MY - 2 \$120,000

The chemical nature of the compounds in which trace metals are present in coal will be studied by means of radioactive tracers. The radioactive compounds will be prepared in situ by neutron irradiation. Tracer compounds, so prepared, will serve to identify the element and will permit the following the compound through purification steps leading to its purification and identification. The nature and properties of metal organic compounds in coal are of interest both to understanding their catalytic and/or catalyst poisoning activity in coal utilization processes.

## 2. CHEMISTRY OF COAL CONVERSION

### 2.1 Heteroatom Removal From Coal by Catalytic Hydrogenolysis # MY - 2 \$120,000

In coal conversion processes involving catalytic hydrogenation, the common elements sulfur, nitrogen, and oxygen need to be effectively removed in order to obtain an optimally useful product. There is, at present, an inadequate knowledge of the rates and modes of removal of these heteroatoms under various catalytic conditions. Phenols and furans, for example, often constitute a significant fraction of a coal liquefaction product. Aniline, pyridine, and other amines can also be present in relatively high concentrations in the liquid product. Current environmental regulations require almost quantitative sulfur removal. The purpose of this research program is to determine the facility with which selected sulfur-containing compounds, polycyclic phenols, and amines can be catalytically reduced under common coal liquefaction conditions. Data for the previously investigated systems involving thiophene and benzothiophene would be used to calibrate the experimental apparatus and to provide a basis for correlation of data obtained with more complex compounds. The initial work would be conducted with commercial Co/Mo catalysts; eventually, other catalysts such as Ni/W and ZnO would be used. During the studies, the role of H<sub>2</sub>S and other compounds in conditioning catalysts will be determined. Data obtained in this study will also permit a better quantification of the temporary poisoning of catalysts by gases such as H<sub>2</sub>S, H<sub>2</sub>O, and NH<sub>3</sub>. The experimental work would involve the use of a pulsed micro-reactor system combined with gas chromatography - mass spectrometry for analysis of the reaction products.

#### Capital Items Required:

- (1) Modification of existing gas chromatograph - mass spectrometer system. Includes purchase of recording equipment, retrofitting electron multiplier, and modifying vacuum system. \$14,000
- (2) Modification of vacuum system to permit use of existing chemical ionization source. \$12,000

### 2.2 Hydrocracking, Hydrogen Addition, and Condensation Reactions in Coal Liquefaction # MY - 2 \$120,000

In an optimized coal liquefaction process, the formation of both light gases and very high molecular weight compounds necessarily is minimized. Thus, the relative rates at which compounds formed under typical coal liquefaction processes are condensed to form heavier compounds or are hydrocracked to form lighter compounds must be known.

## 2.2 Hydrocracking, Hydrogen ... (Cont.)

For example, naphthols (which are known liquefaction products) can be hydrocracked to benzene derivatives or condensed to compounds such as 1,1' dinaphthyl and perylene, depending on the reaction conditions and the catalyst employed. In this investigation the relative effects of hydrocracking, hydrogen addition, and condensation reactions on coal liquefaction product composition and hydrogen consumption would be studied as a function of several variables including contact time, temperature, hydrogen pressure, and type of catalyst. The experiments would be conducted using both coal and model organic compounds. Radical scavengers such as quinones would be used to study the control of condensation reactions. The role of various catalysts in promoting hydrocracking or condensation reactions would also be investigated. The systems involved in these studies would be analyzed using spectrophotometric, mass spectrometric, NMR, and chromatographic methods.

### Capital Items Required:

(1) Fluidized Sand Bath (two)	\$1,000
(2) Transducer, Readout Instrument, Recorder	\$3,000
(3) Temperature Controller and Recorder	\$ 600

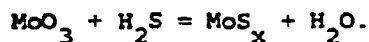
## 2.3 Thermodynamic Data for High Temperature Coal Processing # MY - 2 \$120,000

Extensive thermochemical data are available for low-molecular-weight organic compounds. These data are usefully applied to organic reactions at near-ambient temperatures for liquid phase reactions and at high temperatures for gas-phase reactions. However, thermochemical data for organic compounds in general and high-molecular-weight compounds in particular are not available at the temperatures of interest (300 to 600°C) in coal liquefaction. A major objective of this program, therefore, is to compile enthalpy data for relevant compounds and to estimate free energies of formation utilizing the enthalpy data and calculated entropies. Particular attention would be paid to the compounds known to be formed in high yield in coal liquefaction processes; e.g. polycyclic hydrocarbons, phenols, sulfur-containing compounds, and amines. Some attention would be paid to the thermodynamic characterization of coals. After making an initial compilation and critical analysis of available high-temperature thermodynamic data, experiments would be conducted to establish the validity of the estimated thermochemical data for selected compounds.

Another objective for this program would be to develop thermodynamic data for catalyst systems. The initial effort would be a critical analysis of the phase relations among the molybdenum oxides and sulfides, including consideration of the thermodynamics of the Magneli phases and

### 2.3 Thermodynamic Data ... (Cont.)

estimates of equilibrium constants for reactions such as



Other sulfide equilibria involving elements such as arsenic and titanium which are known to cause poisoning of hydrocracking and hydrodesulfurization catalysts would also be determined.

Information developed in this program would be used to compare the compositions of actual hydroliquefaction streams with those expected under equilibrium conditions.

#### Capital Items Required:

- (1) Combustion calorimeter, including data recording system. \$ 8,500
- (2) Vapor deposition system for thermodynamic studies with catalysts. \$12,000

### 2.4 The Thermodynamics of Coal-Related Hydrocarbon in Solutions at High Temperature # MY - 2 \$120,000

In all the processes for converting coal to liquid or gaseous hydrocarbons, there is involved one or more reacting liquid mixtures containing many degradation or hydrogenation products of coal. In order to predict the course of the reactions which occur in such mixtures, it is necessary not only to know or estimate the heats of formation and entropies of the various hydrocarbons in their pure states, but also it is necessary to estimate their heats and excess entropies of mixing in the reacting solution. It has been possible to correlate with some success the measured excess thermodynamic quantities for mixtures of relatively simple organic compounds with such properties as their molar volume, polarity, and especially their cohesive energy density. Relatively little is known, however, about the thermodynamics of mixtures of the higher molecular weight, polycyclic compounds which are produced by coal degradation or hydrogenation.

We propose, therefore, to investigate the heats and entropies of mixing of selected high-melting polycyclic compounds with solvents typical of those used in coal degradation and hydrogenation processes. The experimental method employed initially would be the precision measurement of the solvent vapor pressure as a function of solution composition. This would be followed by isopiestic or perhaps osmotic pressure measurements depending on the nature of the systems to be studied.



## 2.4 The Thermodynamics of ... (Cont.)

The solutions produced in contact with coal in coal utilization processes have been found, after many years of investigation, to be very complex mixtures indeed, containing many different compounds, some highly polymeric, some extensively associated, and others in numerous isomeric forms. In the presently proposed study, we hope to approach the formidable problem of describing the thermodynamics of such mixtures by beginning with carefully chosen pure substances, determining how they behave in simple mixtures, as a function of their individual physical and chemical properties, and finally extending the resulting correlations to more complicated mixtures.

## 2.5 Modeling of Rearrangements of Coal Precursors and Coal Liquefaction Products # MY - 2 \$120,000

Substances containing the bicyclo[2.2.1]heptane skeleton are an important class of naturally occurring compounds found in pine pitch, turpentine, coal tars, coal ambers, oil shales, fungal toxins, and in certain insects. The skeleton is found in many terpenes. The organic and structural chemistry groups of the Chemistry Division have collaborated successfully to devise an algebraic model which, in connection with computer techniques, has been used to solve specific rearrangement processes or pathways in bicyclo[2.2.1]heptane chemistry. This mathematical system allowed the construction of graphs which serve as road maps for determining sequences of several different chemical rearrangements which the bicyclo[2.2.1]heptane skeleton is known to undergo. The graphing and computer techniques have been applied directly to specific chemical problems, and yielded important information about reaction pathways in every case selected.

The chemistry of the fossil fuels involves an incredible number of organic compounds, but many of them have been studied extensively by organic chemists and biochemists. A fundamental aspect of organic geochemistry, of fuel conversion operations, of coal liquefaction and subsequent processes concerns the network of reactions which takes place. The number of different compounds and reactions is so large that a systematic approach requires the application of computer techniques.

As a joint venture involving the organic chemistry and structural chemistry groups of the Chemistry Division, we propose to undertake an extensive program in mathematical modeling of the major reaction networks involved in organic geochemistry, i.e., in the biosynthesis and geosynthesis of these natural products. The first objective is to model the mechanisms for the formation and inter-conversion of the compounds produced from multiples of the five-carbon-atom isoprene unit, particularly compounds such as the triterpenes and isoprenoid hydrocarbons. These compounds are common, basic constituents of plant

## 2.5 Modeling of Rearrangements ... (Cont.)

materials from which coal and other fossil fuels were derived. The second objective is to apply the same modeling techniques to fuel conversion and coal liquefaction processes. Our recent success in the related project mentioned earlier (first paragraph), and the success of the Corey-Wipke project on computer-assisted design of organic syntheses give us confidence that there is a reasonable chance of success for our proposal.

Associated with the foregoing mathematical modeling project is a study of the fundamental hydrogenation processes which are of topmost importance in coal-energy research. We have already collaborated on a problem in which catalytic hydrogenation of an unsaturated organic compound has been studied by substituting deuterium for hydrogen. Neutron diffraction techniques were used to determine how much deuterium was in every substitutable position in the molecule with high precision ( $\pm 0.5\%$ ).

## 2.6 Fundamental Hydrogenation and Rearrangement Reactions Related to Coal Chemistry by the use of Nuclear Magnetic Resonance Spectroscopy      \$ MY - 2      \$120,00

Nuclear magnetic resonance spectroscopy (nmr) is now one of the most reliable, powerful, and useful techniques for determining the structures of organic molecules, and for locating isotopic substituents in these molecules. Both hydrogen magnetic resonance and carbon-13 magnetic resonance are at present almost universally employed in organic chemical research.

Since all forms of coal, oil, oil shale, coal ambers, and the biosynthesized precursors of coal and oil are made up of organic molecules, nmr spectroscopy can be of extreme value and of topmost importance in solving problems which arise in research involving these materials. We therefore propose the use of nmr spectroscopy and the associated necessary organic techniques to study (1) a variety of homogeneous and heterogeneous catalytic hydrogenation processes of importance in the hydrogenation of coal; (2) several isomerization and molecular rearrangement reactions of the type which occur during subsequent chemical reactions of coal hydrogenation products; and (3) biosynthetic pathways of importance in the production of coal precursors.

### Capital Funds:

- |                                    |          |
|------------------------------------|----------|
| (1) *Fourier Transform             | \$70,000 |
| (2) ** Radio Frequency Oscillators | \$16,000 |

### 3. ANALYTICAL CHEMISTRY

3.1 Chemical Characterization of Materials Used and Produced by  
Coal Hydrogenation Technology # MY - 2 \$90,000

The complete qualitative and quantitative analysis of materials as complex as those used and produced in coal hydrogenation technology (CHT) would be prohibitively expensive in both time and money. However knowledge of the constituents (both inorganic and organic) in these materials is needed as a basis for much of the R/D that is planned for both the engineering and the environmental/health aspects of CHT. At ORNL there exist extensive capabilities for both inorganic and organic analysis, within the Analytical Chemistry and Chemical Technology Divisions. Sampling expertise resides in the Industrial Hygiene Department. We propose to take advantage of these existing capabilities to examine in considerable depth representative samples of input materials, process streams, and discharged materials from CH pilot plants of different types. These samples would then be subjected to multi-element trace analysis by spark-source mass spectrometry, neutron activation analysis, x-ray fluorescence, and other methods as appropriate. The samples would also be subjected to a battery of organic analytical procedures that are now in use for chemical characterization of tobacco smoke and smoke condensate. The most common health-hazardous compounds or classes of compounds would be determined in this examination. Both aqueous and non-aqueous samples would be examined for noxious materials, primarily by gas and liquid chromatography, respectively. Structural identification of selected components will be made as appropriate. The initial product of this work would be a self-consistent set of data pertaining to both inorganic and organic constituents and related to existing pilot plants. The data base would then be augmented by additional analyses for specific compounds or classes of compounds as specific needs are identified by other R/D efforts in CHT.

3.2 Development of Multi-Component Analytical Techniques for  
Coal-Related Materials # MY - 2 \$90,000

The examination and analysis of complex organic and aqueous-organic mixtures is central to many aspects of coal conversion research. Chromatographic techniques of various types are commonly used to separate, identify, and determine constituents in such complex mixtures. By careful design and rigid control of experimental conditions, it is possible to devise procedures that provide analytical information (tentative identities and relative amounts) of many (10 to 100 or more) compounds in a single experiment. Moreover, by judicious selection of sample preparation (class fractionation and/or formation of volatile derivatives) and chromatographic detection (e.g., sulfur- or nitrogen selective), it

### 3.2 Development of Multi-Component ... (Cont.)

is possible to determine only compounds of a given class or those that contain a given element. We have explored the utility of these "chromatographic profiling" techniques with extremely complex organic mixtures deriving from tobacco smoke and smoke condensate, with good results. We propose to develop and apply the profiling approach for coal-conversion studies. Initial effort will be placed on devising and optimizing sample preparation, chromatographic, and detection parameters, in toto, to provide means for quickly examining complex samples for specific types of compounds related to coal-conversion technology. Secondary attention will be given to firm identification by spectral techniques of significant constituents within a given profile, e.g., those that vary with a given reaction or process parameter. Thirdly, we propose to examine the combined use of chromatographic profiling and mathematical techniques for drawing correlations within multi-parameter systems.

### 3.3 Development of Specialized Analytical Instrumentation for Coal Hydrogenation Research # MY - 1.5 \$70,000

Many studies related to coal conversion technology are concerned specifically with sulfurous and nitrogenous compounds. Analytical instrumentation is needed that is specific for these compounds, has good resolving power, is sensitive, and applicable to a variety of sample types. We propose to design, construct, evaluate, and implement the use of such instruments using initially the gas chromatograph in conjunction with element-selective detectors for sulfur and for nitrogen. The use of microwave emission spectrometry as a tunable (but specific) detector for sulfur and/or nitrogen will then be developed. Thirdly, we will study and attempt to develop GC detectors that are selective for other types of compounds that are important in coal conversion technology, e.g., unsaturated compounds, aromatics, and oxygenated compounds. Such instruments, once developed should have wide utility for both research and engineering studies related to coal conversion technology.

#### 4. SEPARATIONS SCIENCE

##### 4.1 Activated Carbon Studies

# MY - 2      \$120,000

Activated carbon seems to provide a unique focal point for energy research, and particularly for coal research. It is probably the cheapest, all-purpose adsorbent available. The residual chars from hydrogenation and liquefaction of coal probably are even cheaper source materials for activated carbon. Activated carbon can be applied to removal of all types of contaminants from solutions. This would include the organic contaminants, including the possibly carcinogenic ones, produced in coal treatment.

Activated carbon is apparently used in Europe in desulfurization of gases. For example, through inherent catalytic activity, it can remove  $H_2S$  from gas streams and allow recovery of the sulfur. Because of this obvious application to serious pollution-control problems, some additional intensive work in this area is needed, including possible modification of the catalytic activity through modifications of the carbons.

Finally, it appears that the techniques used for preparing activated carbon from chars have more than a superficial resemblance to the water-gas reaction. We would hope that eventually a comprehensive program on the kinetic aspects of the reactions of chars with water,  $CO_2$ , and oxygen could be carried out in the hope of clarifying some of the problems related to coal gasification and liquefaction. Since the chars and the activated carbons can also be made from current crops, as well as lignites and coal, it is hoped that such a program might provide a bridge between the currently divergent techniques of preparing, by chemical means, gaseous and liquid fuels from wastes and from coals.

##### 4.2 Multiphase Flow in Porous Bodies

# MY - 1.5      \$75,000

An area of important long-range impact in fossil fuels development is multiphase flow in porous bodies.

This porous body flow is visualized as involving a combination of hydrodynamics and surface chemistry of importance in studies as divergent as catalysis and advanced oil recovery. Since a great deal of work has been done in this field, particularly by the oil industry, it will be necessary to carry out an extensive literature survey and discussions with industry in order to develop a properly focused program. For FY 1975, sufficient funds are suggested to have one senior man work full time in this area. A modest experimental program involving one additional

#### 4.2 Multiphase Flow ... (Cont.)

man could probably be initiated in the second half of FY 1975. Some effort along this line was projected in the 189 entitled "Filtration in Inorganic and Biological Systems" for FY 1976; this would be moved up under this proposal.

#### 4.3 Engineering Sciences

# MY - 1.5 \$90,000

A typical coal hydrogenation reactor has a large length-to-diameter ratio, a configuration which typically leads to gas-bubble coalescence and slugging of the bed. A study is proposed to examine dispersal of the gas and coalescence of the gas bubbles in a three-phase bed as a function of liquid and gas velocity, liquid viscosity, solid particle size and density, and gas introduction technique. This study should lead to a better understanding of the behavior of such three-phase beds and optimization for the best contact of gas, liquid, and solid phases.

Since gas-bubble coalescence is a recognized problem in the catalytic hydrogenation units, an effort will be made to develop a contacting unit which disperses the phases using fixed flow dividing elements. This should ensure optimal contact between the liquid, gas, and catalyst. The introduction of turbulent forces is also desirable to increase mass transfer to and from the catalyst surface and may be beneficial in preserving the catalyst activity by impeding the accumulation of insoluble solids on the catalyst.

A simple system such as irreversible sorption of a dye or radioactive tracer on the solid will be examined to determine the effects of operational variables in the three-phase system on mass transfer.

#### 4.4 Biological Processing of Coal

# MY - 2 \$120,000

Several microorganisms are known to interact selectively with various constituents in coal or in the ash resulting from coal combustion. Such interaction could be the basis for removal of unwanted impurities as well as a means of recovery of valuable components. In general such a process would require size reduction and an aqueous slurry. For example, several species of bacteria including Thiobacillus thiooxidans and Thiobacillus ferrooxidans are known to oxidize and solubilize coal pyrites with the possibility of removal of up to 30% of the sulfur content of some types of coal. Other biological systems are known to absorb, dissolve, or to cause precipitation of many other elements including iron, manganese, and heavy metals. It is conceivable that a microorganism could be found or an existing species could be altered to interact with the primary carbon structure in a way that could produce useful liquid fuels.

#### 4.4 Biological Processing ... (Cont.)

These biological techniques have not been studied seriously in a process mode, and none has been carried out in continuous equipment. We propose to mount a process development effort in which economic process flowsheets can be developed and studied and the effects of various process parameters can be considered. At the same time, a small but important effort will be initiated to investigate new biological systems that may be directly usable in coal liquefaction. Results from this effort could also be applied to oil shale processing, especially for any of the biological systems that could be used to alter the shale structure.

#### 4.5 Filtration Research

# MY - 2      \$100,000

Filtration for solids-liquids separations occurs in several of the flow-sheets for coal liquefaction or other coal conversions, and might advantageously be utilized in many other places, if cheap and reliable techniques were available. Catalyst life in the H-coal process, for example, might be prolonged by removal of solids from recycle product returned to the reactor. Phenolic contaminants might also be removed from aqueous effluents.

Projected filtration approaches are usually based on present commercially available configurations. The separations involve complex systems — oil from clays, metal oxides, and unreacted or partially reacted coal, for example — and chemical interactions profoundly affect performance. Better fundamental understanding of these should make possible substantial improvements in filtration efficiency.

We propose to investigate model chemical systems closely akin to those involved in coal processing. Factors affecting filtration of liquids containing single solids representative of those occurring in coal processing will be studied initially. These factors include relationship of particle size and pore size distribution of the filtering media; effect of surface interactions with other components, already present or added to facilitate filtration; and influence of hydrodynamics. The work carried out under the title "Multiphase Flow in Porous Bodies" will be mutually supportive. We shall draw on experience with difficult-to-filter aqueous solutions, such as sewage treated with coagulants. In particular, the use of movement of solution relative to the filtering interface to slow flux decline from thickening of filter cake will be investigated. On account of difficulty of pumping high-solute-content slurries, it appears better in many cases of interest here to move the filtering surface, rather than the solution, by spinning cylindrical filters (axial filtration), an approach which may be useful in practical application, as well as in research.

#### 4.5 Filtration Research (Cont.)

Experiments with oil-solids systems will progress from studies of simple systems at room temperature with oils in the viscosity range encountered in processes to more complicated mixtures at process temperatures. In decontamination of aqueous effluents, we shall try adding substances to adsorb impurities which are then filtered. This approach has proven promising for removal of toxic materials in other cases. We shall also be concerned with concentration of phenolic compounds to a level for introduction into anaerobic filters, development of which is outlined in another proposal of this set.

#### 4.6 Effluents from Coal Liquefaction

# MY - 3

\$150,000

Coal liquefaction and gasification plants produce waste process water and water generated from the coal itself during processing. An analysis of process flowsheets shows that these wastewaters may be expected to contain a large variety of organic carbon compounds together with sulfur and nitrogen compounds. The wastewater produced during the solvent extraction phase of liquefaction, for example, may have in excess of 5000 ppm of phenol, cresol, and their acids. Other aromatic compounds, similar to those produced from coal tar, should be found in the wastewater. Many of these compounds are known to be toxic to aquatic organisms at levels of a few ppm or less. Some compounds, in particular some coal tar derivatives, are known carcinogens. Others, such as phenols, deleteriously affect the quality of water supply sources at levels of one ppm or less. Before this wastewater is released into a receiving water, it must be treated to remove all but one to ten ppm of dissolved organic matter.

Conventional wastewater treatment plants provide little nitrogen and sulfur removal. They are often unable to treat coal tar derivatives. A new device, called the anaerobic filter, is more readily controlled and more adaptable to the treatment of wastewaters of varying quality and quantity. It provides denitrification for the removal of nutrient nitrogen compounds from the wastewater. It also produces carbon dioxide and methane from the degradation of organic compounds. Preliminary tests indicate that aromatic compound concentrations as low as 1/2-gram per liter can be treated using this method. This represents almost a ten-fold increase in the range of current methods.

We propose adaption and optimization of anaerobic filters for compositions typical of aqueous coal liquefaction effluents.



## 5. CATALYSIS

5.1 The Selection and Improvement of Catalysis Related to Coal Conversion Process Development # NY - 1 \$60,000

The number of variables that must be explored in the development of a practical catalytic process is great enough that potentially valuable ancillary experiments are often omitted, if they must be done by persons responsible for the process chemistry. We propose to do research on typical coal conversion catalysts by selecting two or three simple reactions to be used for routine characterization of catalytic activity. For example, hydrogen-deuterium exchange, hydrogenation, oxidation, carbon-carbon cracking, and other such reactions would serve this purpose. We would supplement the activity determinations by appropriate adsorption measurements, using vacuum microbalance techniques and by measurements of the infrared spectra of adsorbed molecules. Poisoning studies and investigations of new materials expected to have catalytic properties, because of their surface electronic structures, also will be conducted. Information from such research should help explain phenomena observed in the very complex practical situation and might point the way toward improved catalysts.

5.2 Solid State Aspects of Heterogeneous Catalysis Related to Coal Research # NY - 2 \$120,000

Unfortunately, a fundamental understanding of the physics of heterogeneous catalysis does not exist. We propose a program of closely coordinated experimental and theoretical research to provide a better understanding of heterogeneous catalytic action through investigations aimed at correlating the surface geometry and electronic structure of known catalytic materials, as well as that of new materials expected to have catalytic activity. Specifically, we propose to measure and compare soft x-ray and Auger spectra of such materials to determine similarities and differences between corresponding spectra from the conduction bands of these materials in order to develop models which should guide the development of theories regarding catalysis. By means of low energy electron diffraction studies, the role of surface geometry in catalytic processes will be established. Both spectral and diffraction methods also will be used to study the mechanism of poisoning processes and the effects of temperature cycling and environment on this problem - especially the loss of activity. Finally, using data obtained from the above studies, we hope to develop new catalytic materials which are either better, cheaper, or less easily poisoned.

5.3 Mechanisms of Interaction Between Coal and Molten  
Salt Hydrocracking Catalysts # MY - 3 \$180,000

Liquid Lewis acid halides (such as  $ZnCl_2$ ,  $Al_2Cl_6$ ,  $SbBr_3$  and various halide mixtures) are highly active and unusually selective hydrocracking catalysts that convert coal into clean liquid fuels with minimal hydrogen consumption. Although they have been subjected to considerable engineering testing, the basic mechanisms by which these inorganic liquids interact with complex organic materials remains unclear. This project has as one objective a study of coal-catalyst dissolution or mixing mechanisms, which are believed to differ with the type of liquid catalyst and may involve both true solution and organic-inorganic colloidal dispersions. A second objective is a study of the species formed by the dissolution of coal-related organic compounds in liquid catalysts. This study will utilize both nuclear magnetic resonance and optical spectroscopic methods. These have already been tested on some selected systems and it appears possible to obtain quantitative data on ion-molecule equilibria. At a later stage reaction rates will be measured, for example, by Pressure-jump and Temperature-jump spectroscopic techniques. In all aspects of this study special attention will be given to the role of fundamental characteristics which distinguish the various known catalytic materials and appear to be related to the key property of selectivity. Among these characteristics are acidity (as measured by  $pX$ ) and acid "hardness."

5.4 Molten Salts in Coal Utilization # MY 2 \$120,000

ORNL has for some time been engaged in chemical and engineering studies of molten salts. Molten salts have been shown to be useful media and catalysts in several coal utilization processes ranging from hydrocracking to gasification. We would like to focus our attention on the chemistry of nitrogen, sulfur and the ash-forming elements in molten salt catalysts with the objective of developing processes by which these elements can be removed in order that the molten salt catalyst can be recycled. An alternative possibility might be the use of molten salts in rejuvenating heterogeneous catalysts used in coal utilization processes. Related areas of possible research include materials for containment of molten salts, their corrosion reactions, and their decomposition reactions.

5.5 Catalytic and Surface Studies # MY - 2 \$120,000

Heterogeneous catalytic reactions of practical importance involve the gas-solid interface, either directly or as an intermediate to the solid-liquid interface. A quantitative understanding of these reactions is usually hampered by a lack of information concerning adsorbed species

## 5.5 Catalytic and Surface Studies (Cont.)

(products, reactants, intermediates, and poisons) on the catalyst surface. This lack of information is particularly evident for the usual case of reaction at elevated temperatures such as those encountered in coal utilization processes.

A great deal of valuable and basic information concerning such catalytic reactions could be obtained from research using the combined techniques of gravimetric adsorption and infrared spectroscopy. These two techniques, as used in this laboratory, have proven capabilities over wide ranges of temperature (77 - 1000°K) and pressure. In addition to providing a direct measure of the adsorption on a catalyst surface, gravimetric adsorption studies can, in principle, provide data on, e.g., kinetics and displacement of adsorbed species from the catalyst surface. The experimental system is also capable of providing physical characterization (such as specific surface area and porosity) of catalysts. Changes in these physical parameters as a result of reaction can be an important factor in catalysis.

The infrared spectra of species adsorbed on solid surfaces can provide information concerning the structure and bonding involved in the adsorption process. Obviously, the spectra of the gas phase of a heterogeneous reaction could also be monitored to provide data on, e.g., product distribution. It is conceptually possible to identify reaction intermediates by obtaining the spectra of trapped (in a low temperature inert matrix such as solid argon) species that are thermally desorbed from a catalyst surface.

Catalytic research such as this can provide basic information related to the complex reactions involved in coal liquefaction. An obvious example is the water-gas shift reaction used to provide hydrogen for nearly all proposed coal liquefaction processes.

## 6. MATERIALS RESEARCH FOR COAL CONVERSION PROCESSES

### 6.1 Solid Particle Erosion of Metals and Ceramics # MY - 2 \$120,000

There have been few basic studies on the mechanisms of erosive wear and resistance to it. We propose to study this process in single and polycrystalline specimens of both ductile and brittle materials. Effects of crystal orientation, duplex structures (hard brittle surfaces on ductile substrates), and environmental effects will be examined. The combination of corrosion and erosion will receive special attention.

### 6.2 Behavior of Metals and Ceramics in Coal Treatment Systems # MY 2 \$120,000

Many high temperature alloys are particularly susceptible to attack by sulfur compounds. The resistance of ceramic liners or coatings is less well-characterized. We will examine the mechanisms of attack of the components of mixed gases and liquids involved in coal conversion schemes individually and collectively on both metals and suitable high temperature liners on coatings.

### 6.3 Hydrogen Embrittlement # MY - 2 \$120,000

In spite of much research, the fundamental mechanism of hydrogen embrittlement of high temperature alloys is not well understood. A study of the interrelationships of structure, permeation, diffusion, trapping, and embrittlement is proposed. Typical high temperature alloys and hydrogen will be studied first. Later hydrocarbon gases and liquids in contact with metals will be studied. Finally, the effects of such products on a variety of ceramic liners and metal coatings will be defined.

### 6.4 Failure Mechanisms in Reaction Vessels # MY - 2 \$120,000

This study is a logical adjunct to the heavy section steel technology (HSST) program being conducted by ORNL for the Division of Reactor Safety and Research. Techniques developed by that program will be applied to study failure modes in reaction vessels at high temperatures in corrosive environments.

6.5 Mass Transport in Ceramics

# MY - 2     \$120,000

The insulating qualities and mechanical integrity of ionic materials often depend on the stability of the ceramic in a temperature gradient. The first studies in this area are an extension of our investigations of mass transport in nuclear fuels in temperature gradients. Next the added complication of the environment will be studied.

6.6 Deformation and Fracture of Ceramics

# MY - 2     \$120,000

The success of most coal conversion processes depend heavily on the behavior of ceramics as insulators and barriers to corrosive attack. Such materials are exposed to loads over long periods of time at elevated temperature and are subject to sudden temperature changes. Our studies in the creep deformation, ductility, fracture, and thermal shock resistance of nuclear fuels can be expanded to include ceramics of specific interest for coal conversion applications. The equipment and techniques have already been developed. Transmission electron microscopy, Auger spectroscopy, and x-ray diffraction will be used with thermodynamic analyses and property determinations.

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