ASSESSMENT OF LONG-TERM RESEARCH NEEDS FOR
COAL-LIQUEFACTION TECHNOLOGIES

FOSSIL ENERGY RESEARCH WORKING GROUP
(FERWG)

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March 1980

Contract Sponsors: DOE/Office of Energy Research and Fossil Energy.
DOE Program Managers: L. Topper (March-July 1979), R. H. Kropschot
(July-December 1979), J. Powers (December 1979-February 1980). DOE
Contract Number: DE-AC01-79ER10007.

ABSTRACT

The Fossil Energy Research Working Group (FERWG), at the request of J. M. Deutch (Under Secretary of DOE), E. Frieman (Director, Office of Energy Research) and G. Fumich, Jr. (Assistant Secretary for Fossil Fuels), has studied and reviewed currently funded coal-liquefaction technologies. These studies were performed in order to provide an independent assessment of critical research areas that affect the long-term development of coal-liquefaction technologies. This report summarizes the findings and research recommendations of FERWG.

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FOREWORD

During the second year of operation, FERWG was asked by J. M. Deutch (Under Secretary, DOE), E. Frieman (Director, Office of Energy Research, DOE), and G. Fumich, Jr. (Assistant Secretary for Fossil Energy, DOE), to provide an "independent assessment of critical research areas that may impact long-term development of coal-liquefaction technologies." The DOE objectives for FERWG are defined in Appendix A; FERWG membership is listed in Appendix B. The assessment of coal-liquefaction technologies was administered through a DOE contract to the Energy Center at the University of California, San Diego in La Jolla, California.

Members of FERWG performed an extensive schedule of site visits to coal-liquefaction process development units and facilities, as well as to university and DOE laboratories, in order to familiarize themselves with current and planned research programs. Site-visit reports and evaluations, with emphasis on identified process and fundamental research needs, were prepared by participating FERWG members after each site visit. These site-visit reports are reproduced in Appendix C.

FERWG members held numerous discussions with the Under Secretary of DOE, the Director of the Office of Energy Research, the Assistant Secretary for Fossil Energy, members of their staffs, DOE program managers, directors of laboratories and development engineers who are involved in coal-liquefaction research and development (R&D) in both industrial and governmental organizations, and university-based scientists and engineers who perform research related to coal-liquefaction studies. In addition, FERWG received written comments from experts on coal liquefaction in response to the draft letter that appears in Appendix D.

The Executive Summary is followed by an introductory discussion (Chapter 1) in which we present the FERWG study objectives, describe essential operating features of selected coal-liquefaction processes, and summarize the research recommendations derived from our site-visit evaluations. More detailed research recommendations are discussed in Chapter 2. A review and evaluation of coal pyrolysis is presented in Chapter 3.

The costing of coal-liquefaction processes formed the subject of a separate workshop. The results derived from this activity are summarized in Chapter 4.

Our research recommendations cover a wide spectrum of activities in coal-liquefaction technologies, ranging from fundamental science to process engineering. They have not been constructed to satisfy the desires of either the scientist or the development engineer. Adequate research support for programs relating to coal-liquefaction technologies may aid commercial implementation of the right technologies over the long term and should be especially valuable in the definition and identification of technologies that merit commercialization.

The members of FERWG acknowledge, with thanks, the advice and assistance given by many individuals in government, industry and the universities. The following people, among others, have contributed to our discussions, evaluations, and final recommendations:

D. R. Canfield, R. Hamilton, J. Naylor, J. A. Segerson, and J. Ward (SRC facilities at Ft. Lewis, Washington); N. L. Carr, H. G. McIlvried, K. Parimi, R. G. Sperhac, and J. L. Stephenson (Gulf Oil Co.); L. L. Ansell, R. F. Bauman, J. M. Eakman, R. L. Hartgerink, W. N. Mitchell, J. S. Morrison, R. C. Neavel, R. Schlossberg, R. P. Souther, L. Vernon, and S. Zaczepinski (Exxon Research and Engineering Co.); M. Chervanak A. G. Comolli, E. Johanson, P. H. Kydd, and M. Merdinger (Hydrocarbon Research, Inc.); M. Pell, R. T. Struck, J. D. Sudbury, and C. W. Zielke (Conoco Coal Development Company); G. A. Klumb, V. May, and N. Moll (Dow Chemical Co.); R. Quade and J. Watson (General Atomic Co.); M. Farcasiu, W. Lee, P. B. Weisz, and D. D. Whitehurst (Mobil Research and Development Company); J. B. Howard, J. P. Longwell, W. A. Peters, C. N. Satterfield, and P. S. Virk (M.I.T.); R. Blackader, W. Gillespie, E. Grens, H. Heinemann, C. J. King, P. Ross, A. M. Sessler, J. Shinn, G. Somorjai, T. Vermeulen, and K. Westmacott (Lawrence Berkeley Laboratory); A. Davis, N. Deno, P. Given, and W. Spackman (Pennsylvania State University); A. G. Oblad, W. H. Wiser, and R. E. Wood (University of Utah); A. Beerbower (University of California, San Diego); N. O'Fallon (Argonne National Laboratory); R. Nene (Gulf R & D Co.); B. K. Schmidt (Gulf Mineral Resources); G. A. Stuart (Dow Chemical Co.); W. E. Clark (Conoco Coal Development Co.); D. K. Schmalzer (The Pittsburg & Midway Coal Mining Co.); C. L. Oberg (Rockwell International Corporation); R. H. Fischer, R. D. Kropschot, J. Powers, L. E. Topper, and I. Wender (DOE).

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EXECUTIVE SUMMARY

Funding for basic, applied and exploratory studies on coal-liquefaction systems by the Department of Energy (DOE) is not adequate to support the development of technologies for the efficient production of liquids from coals, using direct or indirect coal-liquefaction processes or pyrolysis. There are three principal problem areas that require long-term and stable research support, viz., problems arising in pilot, demonstration, and commercial plants require solutions; developing coal-liquefaction systems require interactive supporting research; innovative and novel research ideas, including new liquefaction concepts, need to be supported. Improved provisions must be made for integrating R&D support within pilot and demonstration plant programs. Contractors should exercise program flexibility to adjust supporting process research in the light of new findings or unexpected occurrence of unforeseen problems. Coal-liquefaction processes require an integrated systems approach in which all aspects of the technologies (coal preparation, hydrogenation, hydrogen production, bottoms processing, liquid refining, etc.) are properly considered and optimized.

We identify below important R&D areas, each of which we believe requires substantial additional funding (i.e., more than \$10⁶/year) and the first three of which we regard as especially urgent:

- Research is needed on each of the following topics: the basic physics and chemistry, structure, composition, and thermochemistry of coals and of model compounds; volatilization; kinetics and mechanisms of bond scission; subsequent free radical and ionic reactions, including reaction steps involving unstable intermediates; transport properties and fluid mechanics of multiphase flows (see Section 2.1).
- Major opportunities exist for improving direct and indirect coal liquefaction through research in homogeneous and heterogeneous catalysis, using either recoverable or disposable catalysts. Fundamental research should concentrate on mechanisms, kinetics and surface chemistry (see Sections 2.1 and 2.2).
- Bottoms processing is likely to limit commercialization of direct coal liquefaction processes (see Sections 2.6 and 2.7). An integrated program of R&D is needed, using bench-scale tests and pilot plants processing up to 100 tons of coal per day. These tests should be used to study gasification, combustion, and coking of residues (see Sections 2.4 and 2.5).

- Scale-up and optimization of coal-liquefaction processes require improved understanding of processing steps, including two- and three-phase flows with heat and mass transfer and chemical reactions (see Section 2.7).
- A review of environmental and health effects has not been performed by FERWG. We are aware of work in this field. We recognize the need for careful studies on methods of analysis and toxicology in order to assure the definition of adequate environmental and health standards. The emphasis should be on determining health effects of the finished products (see Sections 2.1, 2.8, and 2.9) in parallel with development.
- Improved instruments must be developed for the measurement and control of all phases of the coal-liquefaction technologies, including the characterization and control of effluents (see Section 2.6).
- An augmented and integrated effort must be made to solve, control, or avoid the many physical and chemical materials problems that have been encountered in the development of a variety of coal-liquefaction technologies (see Appendix C).
- Additional research is needed on the characterization of a wide range of individual coals for different coal-liquefaction processes and for optimizing the designs of coal-liquefaction processes for particular coals (see Section 2.1 and Appendix C). These studies will require the creation of a carefully selected coal-sample bank.
- Research on rapid pyrolysis of coal (at low and high pressures) and on coke utilization may lead to attractive alternative routes to coal liquids (see Chapter 3). Fundamental research is needed on the escape of pyrolysis products from a coal particle and on their subsequent chemical reactions, both within the particle and in the vapor phase (see Section 2.1 and Chapter 3).
- Basic research is needed on mechanisms to control regressive reactions that lead to high viscosity of vacuum bottoms and to formation of sticky reactor residues. These studies are needed to assure system operability, good product recovery, and long catalyst life (see Section 2.3).

- Fundamental and applied research should be pursued on separations of liquid streams and solids from the reaction products formed during coal liquefaction. These studies are needed in order to improve recycle systems to reduce processing costs. Vapor/liquid equilibria should be better defined, especially in regions near the critical points (see Sections 2.3, 2.4, and 2.5 as well as Appendix C).
- Down-stream refining facilities should be leased or built for experimental refining of coal-derived oils to produce commercially usable liquids for engine development and also for use in turbines and boilers (see Section 2.9 and Appendix C).

CHAPTER 1:

OVERVIEW OF COAL-LIQUEFACTION TECHNOLOGIES; SUMMARY OF RESEARCH RECOMMENDATIONS

The first FERWG study was concerned with coal gasification. This second study is devoted to coal-liquefaction processes. It is apparent that a need exists for the entire spectrum of coal products: solids, liquids, gases. There are many variables which determine the efficiency and cost of production of a given distribution of products.

The objectives of the development of coal-liquefaction technologies have included each of the following: (i) The production of a solid fuel to replace coal in utility and industrial boilers, as exemplified by the SRC-I process. (ii) The manufacture from coal of a substitute for heavy liquid boiler fuel to replace petroleum-derived residual fuels. (iii) The synthesis from coal of a substitute for refinery feedstocks, normally derived from crude oil, for the manufacture of transportation fuels and distillate fuel oils. The synthesis of fuels for transportation applications is currently judged to be one of our most urgent national programs.

1.1 Introduction

There are three generic approaches to producing liquids from coals:

- i. Pyrolysis, which involves the direct thermal decomposition of coals.
- ii. Hydrogenation, which involves the addition of H_2 to the coal structure from the gas phase or from donor solvents and leads to the production of coal fragments.
- iii. Synthesis from CO/H_2 mixtures, which requires gasification of coal to produce the CO and H_2 mixtures. This step is followed by catalytic synthesis.

Pyrolysis is practiced commercially in the manufacture of metallurgical coke for steel making. The liquids are by-products and are coal tars or creosote oils. Liquid yields are normally in the range of 10-15 percent by weight of the coal fed to the coke ovens. Current research on pyrolysis is directed at producing higher yields of lower

molecular weight liquids by several techniques, including the rapid heating of coals followed by rapid quenching of the products and rapid heating of coals with H_2 addition for product stabilization. The major product is coke or char, which is either burned or gasified.

Direct hydrogenation of coal was practiced commercially during the thirties and forties, especially in Germany. Very severe conditions, notably hydrogen pressures of 4,000-10,000 psi, were used in conjunction with mild catalysts (e.g., iron compounds). Relatively high yields of refinable liquids were obtained. The plants had small unit sizes. The costs of liquids produced in this manner is very high. Current research on direct coal hydrogenation is directed at producing high-quality liquids under milder processing conditions by using catalysts and solvents to aid in the transfer of the hydrogen. There are no commercial direct hydrogenation plants in operation; several large-scale pilot plants (100-250 tons/day) have been started up and two demonstration plants (6000 tons/day) are currently being designed. The ranges of temperatures and pressures used in German and in currently developing technologies are shown in Fig. 1.1-1.

The production of liquids by synthesis from CO/H_2 mixtures has been practiced commercially since the thirties, using Fischer-Tropsch technology. This approach is currently used in South Africa (Sasol), where significant capacity expansions are in progress. The overall process efficiency of this route to liquids is low, the liquids produced are broad in boiling range, are relatively expensive. The high costs and inefficiencies are the result of the primary production of synthesis gas. Current research is directed at developing more efficient processes for the generation of CO/H_2 mixtures from coals and at more selective catalysis in the conversion of CO and H_2 to liquids. Advanced processes in both of these areas are currently being considered for large pilot plants and rapid commercialization is anticipated.

1.2 Processing Steps in Direct Coal Liquefaction

All processing sequences used for direct hydrogenation in the production of coal-derived liquids involve the following steps: (i) Addition of hydrogen to supply the needed constituents for the required increase in hydrogen to carbon ratio. (ii) Cracking of the coal in the presence of hydrogen (hydrocracking) to produce compounds of reduced molecular weight. (iii) Removal of sulfur- and nitrogen-containing compounds (e.g., H_2S , NH_3) that have been formed by hydrocracking, as well as removal of water produced by reaction with oxygen atoms contained in the coal. (iv) Appropriate bottoms processing and separation of the desired liquids from ash and any remaining unreacted coals.

Fig. 1.1-1 Identification of pressure and temperature regimes for German and for developing coal-liquefaction technologies.

A generalized flow diagram for direct coal liquefaction is shown in Fig. 1.2-1. This diagram contains the major processing steps that occur in the Gulf Oil Company solvent-refined coal procedure (SRC-II), the Exxon donor solvent process (EDS), and the catalytic Hydrocarbon Research process known as H-Coal.

Reference to Fig. 1.2-1 shows the following processing features. The raw coal is first dried and ground (①) to produce the feed coal that is mixed (②) with a (recycled) solvent to produce a coal slurry to which hydrogen feed is added in appropriate amounts (③). The liquid mixture of coal, solvent and hydrogen is then preheated and dispersed (④) before entering the liquefaction unit (⑤). The liquefier may be a catalytic reactor (as in the H-Coal process) or a thermal reactor (as for the SRC-II and EDS processes). Because of the necessary presence of mineral matter, both in the coal and in the (recycled) solvent, the so-called thermal liquefaction of the SRC-II and EDS processes will also involve catalyzed reactions. After liquefaction, the reaction products undergo a series of separation steps, beginning with gas removal (⑥) and pressure reduction or let-down (⑦) during which low molecular weight hydrocarbons (light ends) are separated. At this point, some of the heavy product may be recycled to the feed slurry, as in the SRC-II process (⑧). However, most of the heavier remaining material is now subjected to one or more processing steps to separate the principal liquid products from heavy liquids and solids (⑨). The latter may be partially pyrolyzed to generate feed hydrogen (⑩) and ash (⑪) while the principal liquefaction products enter a separator (⑫) from which both desired liquefaction products are recovered (⑬) and recycle solvent is bled (⑭) for prior solvent hydrogenation in the EDS process or for direct reuse in the coal slurry (as in a version of the SRC-II process).

The generalized flow diagram of Fig. 1.2-1 is augmented by detailed descriptions of processing sequences in connection with discussions of site visits to individual direct coal-liquefaction processes (see Appendix C for details).

1.3 Indirect Coal Liquefaction (Fischer-Tropsch Synthesis)

The reaction of CO with H₂ to form CH₄ was investigated about 100 years ago. An important discovery was made around 1925 when Fischer and Tropsch succeeded in developing catalysts which yielded straight-chain hydrocarbons from CO and H₂ at atmospheric pressure and relatively low temperatures. However, it took ten years until a practical clean-up system and special reactors could be developed to protect the very sensitive catalyst from poisoning and from overheating. Research followed to replace the tricky cobalt-thoria

Fig. 1.2-1 A generalized flow diagram for direct coal liquefaction (after R. H. Fischer).

catalyst with iron and to design more practical reactor systems operating at medium pressures of 300-400 psi. This work led to commercial application in 1955 in the Sasol plant (South Africa), based on use of activated fused iron powder in an entrained solid circulation system. This system serves as the basis of two 50,000 bbl/day plants which are scheduled to begin operation in 1984, after 25 years of successful liquefaction on a smaller scale. Individual reactors now have about 100 times greater capacity than the fixed-bed units that were first applied in Germany. The Sasol procedure is the only coal-liquefaction process that is available for immediate commercialization with unit scale-up of about a factor of ten. The product slate consists of a mixture of gases, transport fuels, and chemicals. The Sasol process utilizes a Lurgi gasifier that is not suitable for handling either (Eastern) caking coals or coal fines.

Starting with syngas, coal-derived liquids may be processed in a Synthol reactor (as in Sasol II) to produce hydrocarbons (olefins, paraffins) and alcohols containing up to C_{20} .

The key disadvantage in the Sasol process remains the same which characterized the original Fischer-Tropsch work, namely, poor product quality and yield pattern. Work is now being directed toward synthesizing a narrower range of hydrocarbon liquids. The raw product contains a wide range of oxygenated compounds and much of the product falls into the LPG range (C_3 - C_4).

As we have already noted, the principal cost item (70-80%) in indirect liquefaction involves the conversion of coal to syngas, whereas the production of H_2 from syngas followed by the water-gas shift reaction in direct liquefaction processes is generally considered to represent 30-40% of total cost. Thus, the design of efficient gasifiers is even more important in indirect than in direct liquefaction. Commercially available gasifiers include the dry-gas Lurgi gasifier (for non-caking coals), Koppers-Totzek gasifier (an entrained flow gasifier), and the Winkler fluidized-bed gasifier; promising developing gasifiers are the Texaco and Shell-Koppers, entrained flow, partial oxidation gasifiers, which are currently being tested on scales of several hundred tons of coal per day.

A major advance in indirect liquefaction technology is the result of recent developments involving shape-selective zeolite catalysts. Workers at the Mobil Oil Company have tested catalysts of this type with good success on the selective conversion of methanol to aromatic, high-octane motor fuel. Thus, the syngas may be converted to methanol (which is currently produced commercially either by the ICI or by a Lurgi process) for direct use (e.g., in turbine combustors or as an

additive to gasoline) or for conversion to high-octane gasoline or to jet- and diesel-oil using the Mobil shape-selective (zeolite) catalyst system, which has been tested in a 4 bbl/d pilot plant. Compared with Fischer-Tropsch synthesis, 64% higher gasoline yields, 47% higher liquid fuel yields, and 8% higher thermal efficiency have been claimed. It has been suggested that the combination of a gasifier producing syngas with a low $H_2:CO$ ratio (using Koppers-Totzek, Texaco, Shell-Koppers, or Slagging-Lurgi units) with a Fischer-Tropsch slurry reactor and involving an internal water-gas shift reaction may produce an excellent feed for the Mobil catalytic process.

Research on indirect liquefaction seems particularly promising and may well lead to novel and innovative processing techniques. For this reason, it is possible that the indirect route to transportation fuels will turn out to be cost-competitive with the direct liquefaction processes referred to in the preceding paragraph. This last statement is made advisedly and in spite of the fact that indirect liquefaction necessarily entails a significant energy penalty that is associated with the requirement of decomposing the entire coal structure in order to manufacture the raw materials needed for indirect liquefaction. A key issue for any given project will be the quality of coal selected for processing. It is possible that the coal response to gasification or hydrogenation will lead to preferential selection of one of these two routes for liquefaction.

A schematic overview of indirect coal-liquefaction processes is given in Fig. 1.3-1.

1.4 Other Coal-Liquefaction Processes

In addition to the processes described in Sections 1.2 and 1.3, exploratory and commercial work has been in progress on a number of different procedures. These include Conoco's $ZnCl_2$ - "catalyzed" process, Dow's direct liquefaction procedure, variants on the Mobil process, flash pyrolysis, supercritical extraction, extraction followed by hydrotreating, pyrolysis followed by gasification, proprietary systems (e.g., at Exxon), and others. We describe essential features of some of these processes in Appendix C in connection with our site-visit reports.

1.5 Past, Current and Projected Unit Sizes of Direct Coal-Liquefaction Plants

An overview of past, current and projected unit sizes of direct coal-liquefaction plants that have received major DOE support is presented in Table 1.5-1.

Fig. 1.3-1 Schematic overview of indirect coal-liquefaction processes; reproduced from I. Wender.²

Table 1.5-1. Scales and operating schedules for selected direct coal-liquefaction processes .

Process designation	Industrial development	Operating scale in tons of coal per day	Time period
SRC-I	Southern Service Co., Wilsonville, Alabama	6	
SRC-II	PAMCO, Ft. Lewis, Washington	30	1978-79
	Gulf Oil Corp.	6000	mid-eighties
EDS (Exxon Corp.)	Recycle coal-liquefaction unit (RCLU)	2.5×10^{-2}	before 1965
	Coal-liquefaction pilot plant (CLPP-1)	0.5	1965-69
	CLPP-2	1	1975-79
	Experimental coal-liquefaction plant (ECLP)	250	projected: 1980-82
	Commercial-scale demonstration plant	~ 25,000	after 1988
H-Coal (Hydrocarbon Research, Inc.)	Process development unit (PDU)	3.5	1964-79
	Pilot plant	200-600	projected for 1980-82
	Commercial-scale demonstration plant	~ 25,000	probably after 1988

1.6 Comparisons of Direct and Indirect Coal Liquefaction

The Germans made about 80% of their fuels by direct liquefaction during World War II. Their largest plant used about 600 tons of coal per day. This scale is not much larger than the pilot plants that will come on stream in the U. S. and in Germany in the near future. The indirect route, the Fischer-Tropsch process, was more costly and less energy efficient than the direct route. Furthermore, the Germans did not have a good clean-up system for the removal of sulfur from their synthesis gas. Since the Fischer-Tropsch catalyst is highly susceptible to sulfur poisoning, extensive use could not be made of the indirect route in Germany, although plants of this type were built in Manchuria, Japan, and other countries.

After the war, South Africa chose the Fischer-Tropsch process to make synthetic fuels and chemicals. The South Africans have the only commercial plants for coal liquefaction in the world today. This development was not an easy job. More than 20 years of research and development were required to solve innumerable problems concerned with operation of the Lurgi gasifiers, the clean-up systems, the catalytic converters, and the separation of the array of products which contained paraffins, olefins and oxygenated products in a wide range of molecular weights. But they persisted and the larger Sasol II and Sasol III units will be coming on stream in the next few years. Thus, this technology, while it may not be the best, is known and can be implemented immediately in the U.S.

Although 70-80% of the cost of indirect liquefaction is incurred during gasification of the coal (as compared with 30-40% for direct liquefaction), given a clean synthesis gas (medium-BTU gas), the possibilities for its conversion to clean, petroleum-like liquid fuels, to methanol, to synthetic natural gas, and to petro-chemicals (both aliphatic and aromatic) exist. Many large chemical companies are actively engaged in searching for new selective catalysts for use in synthesis gas conversion. The Mobil route from synthesis gas to methanol to high octane gasoline will be tried on synthesis gas made from natural gas in New Zealand. The 100 barrel/day fluid-bed Mobil unit to be built in Germany may be adaptable to produce jet and diesel fuels, in addition to gasoline. The products of indirect liquefaction are essentially devoid of sulfur and nitrogen and would be expected to have a toxicity comparable to that of petroleum.

Two pilot plants using direct liquefaction are being built in the U.S. and one German process should be in operation in 1980. As mentioned earlier, gasification plays a smaller though necessary part in direct liquefaction; hydrogen manufacture is still about 30-40% of the

cost. But direct liquefaction promises to be more energy-efficient and possibly cheaper than indirect liquefaction. There are developments in catalysis that can offer major improvements in this field. A promising approach involves matching a dissolver with a following catalytic unit that deals with a slurry or a solution that is readily amenable to catalytic action. Most poisons and coke-forming constituents must be removed before the catalytic unit.

Direct liquefaction can produce liquid fuels that are no more toxic than fuels produced by indirect liquefaction. Modern upgrading methods, offshoots of petroleum technology, can eliminate essentially all of the sulfur and nitrogen from these fuels and reduce polynuclear aromatics to partially saturated and paraffinic products. There is a danger, however, that the public will not be made aware of these facts. There is currently wide publicity dealing with the carcinogenic properties of the primary products produced from coal by direct liquefaction and little follow-up on the already accomplished upgrading of these substances to clean, environmentally acceptable fuels. The problem may well be a result of the published analysis of intermediates produced by direct coal liquefaction, but these may be handled as easily as similar intermediates in petroleum refineries. It is important that the public is properly informed that questions and answers are openly discussed, and that the solutions are properly presented. This information must be promptly disseminated to allay the public perception that the products of direct coal liquefaction are too toxic to handle.

There is little doubt that both direct and indirect routes to coal liquefaction will be used. Indirect liquefaction has arrived sooner but direct liquefaction may perhaps be the route that will eventually be used to make most of our liquid fuels. Only continued and well-funded research will answer the many questions raised in these debates.

1.7 Summary of Observations Derived from Site Visits

Following an extensive program of site visits and discussions with project managers and program participants, we have previously identified (see Appendix C for details) research needs and opportunities relating to coal-liquefaction technologies. Process-research and basic-research recommendations identified during site visits are summarized in Tables 1.7-1 and 1.7-2, respectively. Elaborations of some of these recommendations are contained in Section 2, where we present more detailed discussions of a number of identified research areas.

Table 1.7-1. Process-research recommendations identified during site visits.

Identified Research Needs	Site Visit(s) [*]
1. Improved designs for pressure let-down valves; improved materials of construction for these valves.	1, 2, 3, 4
2. Improved designs for controlled coal feeds.	1, 4
3. Development of instruments for on-line viscometry of coal slurries.	1, 2, 3, 4
4. Design and development of reliable pumps for handling vacuum-tower bottoms.	1, 2, 3, 4
5. Development of a technique for measuring <u>in situ</u> build-up of coke formations.	1, 2, 3
6. Improved instruments for slurry-flow measurements, for identification of water-oil interfaces, and accurate sensors for line openings and closings.	1, 3
7. Identification of operating variables that lead to repolymerization and plugging in pre-heaters and dissolvers.	1
8. Development of improved materials to withstand chloride corrosion in vacuum distillation systems and wash columns.	1
9. Definition of allowable operating variables for sustained controlled dissolver or hydrogenation operation.	1, 4
10. Development of quantitative reaction models for component processes; definition of important observable parameters and design of control units for successful operation.	1, 2, 3, 4, 5, 6
11. Studies on the relation between coal-parameter characterizations and processing ease and output.	1, 2, 3, 4, 5, 6

Table 1.7-1. (Continued)

Identified Research Needs	Site Visit(s)*
12. Studies of the influence of selected catalysts on coal liquefaction.	1, 2, 4, 5, 6
13. Systematic studies on solvent effects in coal-liquefaction.	2, 3, 4, 5, 6
14. Identification of composition and role of recycle materials, including heavy solubilized substances containing mineral matter.	2, 3
15. Studies on solvent fractionation and hydrogenation	1, 3
16. Studies on operating variables that determine product specifications, including allowable concentrations of sulfur, nitrogen, and mineral matters.	3
17. Development of improved procedures for separating ash from coal liquids.	3
18. Identification of the relation between catalyst type and (a) product slate and (b) vacuum residue output in the H-coal process.	4
19. Development of improved coal-liquefaction catalysts that are stable against coking and deactivation.	4
20. Development of processes to reduce hydrogen consumption during coal liquefaction, e. g., through coal pretreatment, slurry preheating to high pressure, etc.	1, 2, 3, 4, 5, 6
21. Development of materials and components needed for long-term operation of molten-salt (e. g., ZnCl_2) processes for direct coal liquefaction.	5
22. Physical and chemical properties should be determined systematically for feed coal and for all multi-phase processing components that are formed during coal liquefaction.	1, 2, 3, 4, 5

Table 1.7-1. (Continued)

Identified Research Needs	Site Visit(s)*
23. Design and development work should be done on more efficient and smaller scale deasphalting units, following the seemingly successful technique described for the Dow deasphalting units.	6
24. Careful process costing should be performed for designs using nuclear heat in coal liquefaction.	7

* Legend for Site Visits: 1, SRC Facilities at Ft. Lewis, Washington (May 11, 1979); 2, Gulf Oil Research Laboratory, Harnmarville, Pa. (October 2, 1979); 3, Exxon Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas (July 13, 1979); 4, Hydrocarbon Research, Inc., Lawrenceville, N. J. (August 16, 1979); 5, Conoco Coal Development Company, Library, Pa. (October 21, 1979); 6, presentations to FERWG at UCSD by staff members of the Dow Chemical Company, Midland, Michigan (November 19, 1979); 7, presentations to FERWG at UCSD by staff members of the General Atomic Company, La Jolla, Ca. (November 20, 1979); 8, Research and Development Department, Mobil Research and Development Department, Mobil Research and Development Corporation, Princeton, N. J. (August 16, 1979).

Table 1.7-2. Basic research recommendations identified during site visits.

Identified Research Needs	Site Visit(s)*
1. Studies should be performed on the mechanisms and rates of bond ruptures in coals.	1, 2, 3, 4, 5, 6
2. The mechanisms of catalysis occurring during coal hydrogenation (e.g., in ebullating beds or in the Dow process) for a variety of catalysts should be studied; relations between catalyst type and structure and product slates for selected coals should be investigated.	1, 2, 3, 4, 5, 6
3. A broadly-based, long range research program should be supported to identify catalysts for indirect coal liquefaction. These catalysts should be characterized by high product selectivity and by high conversion efficiency.	8
4. Fundamental studies should be performed to define the chemical processes that occur during direct coal liquefaction in the presence of selected molten salts. These investigations should yield acceptable models for the slate of products and for process selectivity.	5
5. Fundamental studies should be performed on physico-chemical processes (e.g., Marangoni effect) that limit the efficiency and determine the sizes of deasphalting units.	6
6. Identification is needed of mechanisms and rates of reaction processes occurring during the hydrogenation steps in coal-liquefaction processes.	1, 2
7. The mechanisms and rates of regressive reactions (repolymerizations) occurring during coal liquefaction should be identified.	1, 3
8. Mechanisms and rates of coke formation in pipes should be elucidated.	1, 2

Table 1.7-2. (Continued)

Identified Research Needs	Site Visit(s)*
9. The development of a convenient procedure is needed for the measurement of the extent of coal oxidation that has occurred.	3
10. Scaling and modeling of coal-liquefaction processes should be studied in adequate detail, including quantitative descriptions of the interactions between fluid flows and chemical rate processes.	1, 2, 3
11. The development of rheological models is recommended for coal slurries, vacuum bottoms, and other multi-phase systems that are encountered during coal processing.	1, 3, 4
12. The mechanisms of chloride corrosion of hastalloy and other materials should be investigated.	1, 2

*See the footnote to Table 1.7-1 for explanations of numerical entries.

The research needs identified by FERWG during site visits are generally consistent with research needs recognized by DOE contractors. Process research needs often refer to urgent practical difficulties that are best resolved by studies performed at contractor organizations in conjunction with current development programs. Our listing does not indicate priorities and we have not attempted to assign appropriate budgetary requirements. Table 1.7-1 is best understood in connection with the site-visit descriptions assembled in Appendix C. While needs and deficiencies identified by FERWG in ongoing programs have greatly influenced our selection of research recommendations summarized in Chapter 2, the basic studies which we recommend have a larger focus than the resolution of ongoing programmatic difficulties. Research on coal science, just as basic research in other fields, should be of such a scope that its effective prosecution will yield results that will be useful in applications that are not now defined while serving, at the same time, as a repository of knowledge that may serve to resolve or ameliorate ongoing programmatic difficulties.

CHAPTER 2:

RESEARCH RECOMMENDATIONS

In this chapter, we present detailed research recommendations dealing with the following topics: basic research on coal structure and chemistry, the role of catalysis, regressive reactions, separation technologies and coking, generation of hydrogen and fuel gas from residues, instrumentation and control, scaling and modeling of liquefaction units, and hydrofining of coal-derived liquids.

2.1 Basic Research on Coal Structure and Chemistry

We discuss the following topics: coal characterization, coal chemistry and liquefaction, pyrolysis of coal, catalytic effects in pyrolysis, dissolution of coal, catalytic effects on coal reactions in a solvent, and reactions of coal with gaseous hydrogen in a solvent.

2.1.1 Coal Characterization

Coal is often described as a sedimentary organic rock in order to emphasize its complex and hybrid nature. The major components of coal, roughly 90%, are macerals (i.e., organic substances from plants that have been altered by biological decay and geological processes). Roughly 10% of most U.S. coals is a melange of inorganic compounds, usually referred to as mineral matter. These constituents are held together in a complex physical structure with variable pore sizes and surface areas. In spite of an enormous amount of work, much of which is summarized in recent reviews, our understanding of the organic and inorganic parts of coal and the physical structure of coal is inadequate for a detailed understanding of current technologies. We list here specific research areas, which should lead to improved coal characterization. We suggest research topics but avoid the choice of specific characterization techniques.

A. Characterization of Organic Constituents

The organic part of coal is too highly variable to determine its structure in the sense that organic chemists usually reserve for this word. We need to distinguish carefully between the concepts of composition and structure. What is required is a characterization of coal in terms of typical constituents, especially those that affect reactivity or utility in different processes. Research is suggested on:

- (a) The origin and geologic history of coal. Have the original plant compounds been altered beyond recognition or will

phytochemical models serve as a useful starting point for thinking about coal?

(b) The physical nature of coal: Is it a polymer, a gel, or a mixture of solids? What is the nature of the repeating unit if it is a polymer. What is the extent of crosslinking and its consequences? How could a "molecular" weight be determined? How do coal structures rupture on heating?

(c) Methods of coal classification: There seems to be dissatisfaction with standard petrographic schemes and several groups are working on new methods of classification. Extensive studies are needed of many different types of coal by a variety of physical and chemical techniques. The behavior of coals in various processes must be understood and utilized in liquefaction.

(d) The chemical characterization of coal-derived liquids should include the following studies: the distribution of C and H; the ratio of aromatic to aliphatic segments; the nature and distribution of connectivities; the distribution of polynuclear aromatic hydrocarbons; the distribution of heteroatoms (O, S, N) in coal; methods of determining O, S and N concentrations. The currently available techniques for N analyses are inadequate. Nitrogen compounds appear to be important in asphaltene behavior; oxygen compounds are responsible for high viscosity liquids in some processes.

B. Characterization and Catalytic Behavior of Inorganic Constituents

There has been a recent intense interest in the mineral matter contents of coals because of their potential catalytic activity. This activity has served to emphasize how inadequate our present understanding is. The following studies are recommended: the development of methods to characterize minerals in coal; the behavior of these minerals in coal-liquefaction technologies; the catalytic cycles in which minerals participate; the use of inexpensive minerals as disposable catalysts; mineral-catalyst recycling and recovery; ash disposal; separation of ash from coal-derived liquids.

C. Physical Characterization

Research is recommended on the development of reliable methods to measure surface areas and the distribution of pore sizes because these are known to affect combustion behavior and they are also expected to influence other physico-chemical properties during processing and conversion.

2.1.2 Coal Chemistry and Liquefaction

Coal has been subjected to a variety of treatments that yield liquid product. While this field is very old, vacillating fuel requirements of society have led to either neglect during times of plenty or to crash programs during shortages. Perhaps for this reason, much of the fundamental chemistry involved in coal liquefaction remains to be explored. Our understanding of the kinetics of coal reactions is in a very rudimentary state. Kinetic equations are generally written only for reactants. The mechanisms of these reactions are not known and hence intermediates, such as free radicals, cannot be properly taken into account in kinetic studies. It is important to note that kinetic control, rather than thermodynamic constraints, often dominate reaction processes. The major process variables are temperature, solvents, catalysts, and added hydrogen. We have organized our selection of long-term research needs along these lines.

2.1.3 Coal Pyrolysis

Chapter 3 on Coal Pyrolysis contains a brief discussion of our current understanding of the chemistry involved. Research is recommended on the following topics:

- (a) the reactions that occur for pure coal macerals in given temperature intervals; the types of bonds that break and the rates of breakage in given temperature intervals;
- (b) the subsequent reactions (propagation and termination) of the free radicals formed;
- (c) the mechanisms of these reactions and the ratios of rates for different pathways;
- (d) the extent to which the reactions occur homogeneously or heterogeneously;
- (e) the extent of free-radical diffusion in the coal structure;
- (f) the effect of coal-particle size, coal-particle pretreatment (e.g., oxidation), moisture content, and pore size distribution;
- (g) the changes in coal structure that accompany pyrolysis and the mechanism of char formation;
- (h) the selection of appropriate model compounds for coal research.

2.1.4 Catalytic Effects on Pyrolysis

Research is recommended on the following topics:

- (a) the effects of natural (coal mineral matter) catalysts on any of the reaction steps;
- (b) the functions and mechanisms of other catalysts.

2.1.5 Dissolution of Coal

Research is recommended on the following topics:

- (a) the equilibrium solubilities of coal in various solvents;
- (b) the rates of solution in different solvents;
- (c) the effects of temperature and pressure on the equilibrium solubilities and rates of dissolution;
- (d) the roles of colloidal suspensions;
- (e) solubilities of the initial products of dissolution in reactor liquids.

2.1.6 Reactions of Coal in a Solvent without Catalyst

We recommend research on each of the areas listed under 2.1.3.

2.1.7 Catalytic Effects on Reactions of Coal in a Solvent

Research on each of the topics listed under 2.1.4 is recommended.

2.1.8 Reactions of Coal in a Solvent with Hydrogen Gas

Research on each of the topics listed under 2.1.3 is recommended. In addition, studies should be performed on the kinetics and mechanisms of hydrogen transfer.

2.1.9 Catalytic Effects on Reactions of Coal Solvent with Hydrogen Gas

Research on each of the topics listed under 2.1.4 is needed. In addition, studies should be performed on catalytic effects on the kinetics and mechanisms of hydrogen transfer.

2. 1. 10 Reactions of Coal in a Donor Solvent with Hydrogen Gas

Research on each of the topics listed under 2. 1. 9 is recommended.

2. 1. 11 Catalytic Effects on the Reactions of Coal in a Donor Solvent with Hydrogen Gas

Research is needed on each of the topics listed under 2. 1. 9.

2. 1. 12 Role of Solvents

Typical solvents are frequently of ill-defined composition and very little quantitative information is available on their actions. Research on the following topics is recommended:

- (a) the general types of solvents which are useful and better methods for their characterization;
- (b) the physico-chemical changes of solvents during different processes with special attention to degradation, polymerization and rehydrogenation of donor solvents;
- (c) the incorporation of solvents into final products and the mechanisms of incorporation;
- (d) reactions with components of solvents and dry coal.

2. 1. 13 Other Catalyst Research

The primary processes in coal liquefaction appear to be thermal and are not subject to control by current catalysts. Research on the following topics is recommended:

- (a) a search for catalysts which will affect primary liquefaction reactions;
- (b) catalysts that can be employed to change the final composition of the liquid product and, especially, the problem of hydrodenitri-fication.
- (c) Catalysts that function in a gas-to-liquid technology could well provide useful information about better catalysts to take coal apart.
- (d) We also urge continued work on shape-selective catalysts for gas-to-liquid technologies and novel catalytic systems such as ZnCl_2 .

2.1.14 Stability of Coal Liquids

Many coal-derived liquids are unstable and show an annoying tendency to form high viscosity products. Research is recommended on the mechanisms of viscosity increases for coal-derived liquids.

2.2 The Role of Catalysis

2.2.1 Introduction

Catalysis appears to play a significant role in many coal-liquefaction processes, whether a catalyst is intentionally added or not. On a molecular scale, a catalyst can act to enhance cracking and hydrogenation of the coal itself or of the initially formed coal liquids. Based on petroleum experience, improved catalysts offer the potential to increase liquid yields from coal significantly, while lowering gas production and hydrogen consumption. More energy-efficient processes could also result. Although the mechanism of catalyst action in coal liquefaction is not understood, many process configurations and catalyst forms are being employed in an attempt to optimize the benefits of catalysts. Among the most important are the following:

- (a) disposable or non-disposable catalysts, either naturally occurring or intentionally added and functioning in the liquefaction reactor (H-Coal, SRC, Dow);
- (b) catalysts functioning in a separate reactor (EDS);
- (c) molten-salt catalysts (Consol ZnCl_2);
- (d) soluble or gas-phase catalysts (H_2S , cobalt octacarbonyl).

Downstream refining of heavy coal liquids presents new catalyst challenges. Molecular distribution, heteroatom content, and catalyst poison type and level are significantly different for heavy coal liquids, and catalyst performance cannot be predicted from extrapolations of petroleum data.

In this section, the state of knowledge and research needs in the area of catalytic coal liquefaction and coal liquids upgrading are outlined separately.

2.2.2 State of Knowledge on Catalytic Coal Liquefaction

In this section, we identify important process development and exploratory work. The references¹⁻²⁵ should be consulted for detailed information; for reviews, see Refs. 1-8.

H-Coal⁹ - An ebullating bed of Co/Mo on Al₂O₃ extrudates is used. The small size of the coal solids allows continuous separation from the catalysts. The catalyst consumption is about 1-2 lbs/ton of coal.

Synthoil¹⁰ - a fixed bed of Co/Mo is used on Al₂O₃ extrudates. High slurry mass velocities are employed to keep the catalyst free from ash. The catalyst consumption is 1-2 lbs/ton of coal.

SRC¹¹ - The iron in the ash is considered to be catalytic. Recycle mineral matter and added iron are being investigated as catalysts.

Dow¹² - One-micron particles of MoS₂ are slurried with coal and coal liquids. Two lbs of Mo/ton of coal are present in the reactor. Recycle of coal liquids reduces Mo makeup to ~ 0.5 lb Mo/ton coal.

EDS¹³ - Catalyst is not added in the liquefaction reactor. The Co/Mo on Al₂O₃ catalyst partially hydrogenates and fractionates coal-liquids in a recycle stream. The catalyst consumption is ~ 0.2 lb catalyst/ton of coal.

Consol¹⁴ - The ZnCl₂ melt (2:1 weight ratio of ZnCl₂ to coal) is a catalytic medium for coal liquefaction at low temperature. Combustion to ZnO is the preferred method for melt regeneration.

University of Utah¹⁶ - ZnCl₂ (~ 10 weight percent on coal) is a preferred catalyst for a high temperature, low-residence time liquefaction process. The catalyst is recovered with an HCl wash.

Ruhrkohle/Bergbauforschung - This is a pilot-plant development of a low-pressure version of the Bergius, iron-catalyzed coal-liquefaction process.

The catalytic role of pyrite and other coal minerals is being investigated extensively in the United States.¹⁷ Extensive work in Germany, Britain, and the United States prior to 1945 showed significant catalytic activity for iron, tin, and molybdenum.¹⁸ Exploratory studies of dry hydrogenation of coal indicate that Mo, Co, Ni, Zn, and Sn significantly enhance conversion at levels of 1000 ppm on coal.¹⁹ Exploratory studies of more than 100 inorganic compounds show that tin, nickel, and zinc halides are among the best catalysts.²⁰ Cobalt octacarbonyl is an example of a soluble or gas-phase catalyst. It is highly active for coal liquefaction at low temperatures.²¹

2. 2. 3 Research Needs

Considering only the desired molecular transformations, many of the research needs are identical for coal liquefaction and for coal-liquids upgrading. However, the solid state and high mineral matter contents of coal define major chemical and physical constraints that are not present in liquids upgrading. In general, research in these areas should involve model compounds, carefully chosen and carefully handled coal samples, kinetic studies, tracers, advanced analytical tools, and combinations of these approaches.

A. Research Needs on Catalytic Coal Liquefaction

Catalysts in coal liquefaction may serve the following functions: accelerate the breaking of selected bonds in the coal structure; enhance hydrogen transfer to reaction intermediates; promote hydrogenation of the coal structures, thus making it easier to convert coals to liquids; promote hydrogenation of coal liquids by converting them to donors which can supply hydrogen for the liquefaction process; increase hetero-atom removal; inhibit polymerization and other retrograde reactions. Major research needs relating to catalytic liquefaction of coals are identified in the following statements.

- (a) A critical need in developing a better catalytic liquefaction process is a better characterization of feed coals and liquid products.
- (b) We require development of better understanding of the mechanisms of the catalytic reactions involved in the liquefaction of coal by determining the effects of pore size, porosity, active metal dispersions, and surface chemistry; also needed are measurements of catalyst life and of causes of deactivation.
- (c) Identification is needed of catalytic materials that will selectively break bonds in the coal structure. For example, moderately strong acids with high poison tolerance and low coking tendency should be identified.
- (d) Identification is required of catalysts that enhance hydrogen transfer and that prevent polymerization.
- (e) Identification is required of homogeneous catalysts (gas or liquid phase) with hydrogenation/cracking activity. These catalysts must have the potential for intimate coal-catalyst contacting and open up novel methods for catalyst recovery, such as energy-efficient supercritical phase changes.
- (f) Identification is needed of noncorrosive, easily regenerable, molten-salt catalysts.

(g) Development should be supported of inexpensive materials for containing molten-salt catalysts.

(h) Identification is needed of a coal-conversion catalyst that is effective at relatively low concentrations (e. g., ~ 100 ppm) and at lower temperatures (~750-850°F) and pressures (15-1000 psi).

(i) Identification is required of a coal-conversion catalyst that is chemically stable and does not deactivate rapidly in a coal-liquefaction environment.

(j) Developments of coal-conversion catalysts that are easily recovered and regenerated should be supported.

(k) Studies should be performed to define facile recovery chemistry for known coal-conversion catalysts such as molybdenum.

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2.3 Regressive Reactions

In processes for donor solvent liquefaction of coals, the "progressive reactions" that lead to a desired product must compete with "regressive reactions" tending toward troublesome "muck" phases. Even under the best of conditions, effluent from a liquefaction reactor contains solids comprising mineral matter and unreacted organic matter arising from inert macerals such as fusain. Such solids are, in general, accompanied by a sticky, gummy, pseudo-crystalline matter (mesophase) that arises in the reactor from vitrain. Pyridine-insoluble substances in reactor effluents are well described as "muck phases".

Mesophase often acts as a "glue" to bind reactor solids, minerals and organic material into conglomerates. If these conglomerates remain in a reactor for a sufficiently long time, some of the mesophase reacts further to become a solid semi-coke. Another "glue" sometimes arises from organically bound metals in coal. Calcium "humates" react to form calcium carbonate, and organically bound silicon and titanium react to form the oxides.

Reactor conglomerates can grow so large that they accumulate near the bottom of the liquefaction vessel, and must be purged periodically from the bottom. When catalyst pellets are present in the reactor, as in the H-Coal Process, reactor solids may accumulate on catalyst surfaces (both external and internal) and cause the catalyst to become inactive. It is important to understand how the cooling or heating cycles cause regressive reactions which adversely affect solids-separation methods. The design of a piping system to carry reactor effluent to equipment for product recoveries and separations must avoid stagnant zones where the effluent could react further regressively to form solid plugs within such zones. In other words, the effluent must be kept moving.

In view of the importance of muck phases for system operability, product recovery, and catalyst life, there has been surprisingly little study of the chemical details of regressive reactions. Basic research on understanding and controlling the formation of muck phases is needed.

2.3.1 Background for Research on Muck Phases

In bench-scale work, Whitehurst et al.¹ have studied solvents of varying donor "quality" and have obtained results showing the importance of the donor solvent in suppressing regressive reactions. Kang et al.² have provided practical data illustrating this point from

pilot-scale operations. There has been less tendency for deposits to form in equipment downstream of pilot-liquefaction reactors when heavy moieties that are non-distillable in a vacuum distillation are recycled to the reactor. This observation is consistent with the recently emerging view that such moieties are good "shuttles" for hydrogen from the gas to the liquid phase, although other explanations have also been given (see below). Kang and Johanson³ have discussed the role of coke deposits in deactivating catalysts in the H-Coal Process. They reported an H/C ratio of 0.5 for coke deposits in two large pilot units and gave evidence to support the view that this ratio does not vary greatly with time, i. e., that the coke deposits are not subject to carbonization after they are laid down.

Kang et al.² cited pilot-scale operation in which an increase in reactor temperature, other factors remaining equal, resulted in deterioration in solvent properties. This behavior may support² a hypothesis that coke formation results when thermal cracking "gets ahead" of hydrogenation of the coaly matter by hydrogen transfer from the donor solvent. Whitehurst et al.¹ concluded from bench-scale carbonization tests performed on various SESC fractions that asphaltols (pre-asphaltenes) may be the main source of semi-coke. Asphaltols are rich in chemical functionalities, and some of these species may readily cross-link or polymerize. They contain hydrogen at a higher H/C ratio than the value 0.5 cited above for catalyst coke deposits; therefore, the formation of these deposits may not simply involve polymerization of asphaltols. We recognize from this comparison that there may be more than one mechanism for the production of semi-coke in donor-solvent liquefaction.

From examinations of reactor solids, Neavel,^{4,5} Walker et al.,⁶ and Mitchell et al.⁷ reported anisotropic carbon of a type that pointed to the presence of domains of mesophase in reactor muck phases.

Marsh⁸ defines mesophase as "a liquid crystal of hydrocarbonaceous matter undergoing cross-linking, " i. e., it is a "polymerizing" liquid crystal. If a pitch is heated slowly, tiny domains of liquid crystal appear around 410°C. The formation is reversible: a tiny domain formed at 410°C can be removed by carefully and quickly heating the pitch to 415°C. The domain reappears on cooling the pitch to 410°C, and one can repeat these purely physical transformations several times. On further slow heating, permanent domains of mesophase appear. The mesophase domains grow to a size characteristic of the pitch. A polycondensed, heteroatom-free aromatic species such as anthracene gives rise to relatively large domains. Large molecules rich in functional groups, such as asphaltols, produce smaller domains;

"polymerization" occurs sooner and maintains high viscosity, while the liquid crystals remain small.

The process of formation and growth of mesophase domains can be followed during the slow heating of a pitch by monitoring viscosity. This falls sharply at first. In a pitch giving rise to small domains of mesophase, the viscosity remains low over a relatively narrow interval of temperature and then rises sharply upon further heating. A pitch that holds large domains of mesophase exhibits a low viscosity over a wider temperature interval. The viscosity rises sharply only after substantially all of the pitch is transformed to mesophase during a temperature interval in which "polymerization" proceeds rapidly to convert the mesophase to semi-coke. A discontinuity in the viscosity curve often appears roughly in the middle of the temperature interval for low viscosity. This is an artifact produced by a rotating viscometer and signals the development of a binary system: high-viscosity mesophase spheres in low-viscosity pitch. At first, the spheres are strung out by the dynamic viscosity measurement and thus produce the blip. Later on, the spheres just go around together, causing the viscosity result to fall back. Lamellar aromatic molecules are stacked parallel to the equator of a spherule of mesophase, i. e., the growth of the spherule does not occur in layers like those of an onion.

Shibaoka⁹ reported that mesophase arising from vitrinite hydrogenated in the presence of stannous chloride can be reconverted to liquid and gas by raising the temperature. In his system, mesophase having an H/C ratio of 0.4 or less arose from an asphaltene phase having an H/C ratio of about 0.9. High molecular weight is not a requirement for mesophase formation. Montgomery¹⁰ reports mesophase formation in tests for hydrotreating an aromatic gas oil.

Some semi-cokes show no evidence of birefringence. German workers on the catalytic hydrotreating of tars derived from coals termed such material "asphaltene-derived coke." Other semi-cokes show birefringence in the form of flow structures or rosettes. German workers called these "oil-derived cokes." They can be made from a gas oil, but they can also arise from heavier oily matter.

Marsh⁸ points out that anisotropy in carbons derived from coal can arise from three mechanisms: (1) the mesophase mechanism; (2) preservation of anisotropy present in the raw coal (this may happen when a bituminous coal is oxidized, preventing fluidity); (3) anisotropy arising from pyrolysis.

In a carbonization experiment with slow heating, a bituminous coal of high rank gives rise to large mesophase domains, producing a coarse

mosaic of anisotropic domains of semi-coke. A good metallurgical coke, for example, will produce coke domains larger than about 5 micrometers. Coals of intermediate rank yield finer mosaics, and coals of low rank give no mosaic at all. Residues from donor-solvent liquefaction of a bituminous vitrinite are complex. Petrographic examinations⁷ of such residues identified unreacted vitrinite, granular residue, pitch, and cenospheres, as well as mesophase and semi-coke. "Reactor residues" from the H-Coal Process were reported¹¹ to have an H/C ratio of 1.0. This ratio appears to be inconsistent with an earlier report³ of an H/C ratio of 0.5 for catalyst coke deposits. It appears that much may be learned by systematic study of the H/C ratio of the petrographically-identifiable carbon phases in donor-solvent liquefaction residues.

Important conclusions have been drawn⁶ from inspections of residues during a period of "off" operation in an SRC pilot plant, when the coke yield was so high as to force a shutdown. The inspections showed that anisotropic carbon had grown onto undissolved solids, including mineral matter, fusinitic material, and a coke contaminant that was traced to poor control of the purity of the coal feed. The anisotropic carbon had bonded the undissolved solids together into intractable deposits. It was suggested that plastic, adhesive mesophase had coalesced and flowed over surfaces of inert solids. In time, the mesophase had altered to non-plastic semi-coke.

It has been noted by Montgomery¹⁰ that German practice in the hydrogenation of both high-temperature and low-temperature coal tars was to add "Grude," an extremely fine fly ash containing carbon and arising from the Winkler fluidized-bed gasifier. The purpose of this practice was to control the growth of mesophase domains in reactor muck phases. The addition is believed¹⁰ to coat tiny spherules of mesophase, as they first form, with a "dry" solid, thus preventing the spherules from agglomerating and growing in size. Work on hydrogenation of heavy oils suggests¹⁰ that there may be an advantage in conducting coal liquefaction in a "dirty" reactor, i.e., one with a high concentration of fine, "dry" solids. German additions of "red mud" to coal-liquefaction systems may be mentioned. These additions may well have served to add finely divided "dirt" for mesophase control, as well as to introduce iron oxide. The H-Coal process has always operated with a reactor containing some finely divided mineral matter, which is introduced by a stream that is recycled to the reactor overhead from a hydroclone acting to concentrate mineral species in a portion of vacuum bottoms. Montgomery¹⁰ suggests that one of the functions of the recycle of reactor products in the SRC II process is to build up the concentration of fine "dirt" for mesophase control. There may be a preferred mineral species for this objective. What is the relative importance of this function of recycled mineral matter in the SRC II process in

comparison with catalytic effects of such matter? What is its importance in comparison with effects arising from an increase in the concentration of heavy moieties that are good hydrogen shuttles? Bench-scale experiments to answer these questions may be worthwhile.

Studies¹⁰ of hydrogenation of heavy oils, gas oils, bitumens from tar sands, and the like, often use a specially prepared "dirt" for mesophase control. About 2% of a dried, fine subbituminous coal or lignite are added; on these, Montgomery¹⁰ has sprayed a solution of ferrous sulfate. In the hydrotreating reactor, this species is reduced to ferrous sulfide, which migrates along cracks into the micropores of the fine solid. This species may catalyze hydrogen transfer in the oil phase and hold down mesophase formation from the oil.¹⁰ The presence of a catalytic species in fine solid particles adhering to the surface of a mesophase spherule may even catalyze its reconversion to fully-fluid, oily matter. Montgomery concurs with Shibaoka's finding⁹ that mesophase, at least in the earlier stages of its development toward semi-coke, is liable to reconversion through the action of hydrogen. Montgomery has experienced trouble because mesophase gummed up his reactor; also, coking recurred on walls even when mesophase formation amounted to only about 0.5% of an oil feed to hydrotreating.

"Simple" aromatic oils "wet" coal better than alkylated matter. Petroleum pitches (e.g., a vacuum residue) do not penetrate coal as well as a catalytic cracker recycle stock. This observation may be related to the power of a dried subbituminous coal or lignite to act as a getter for material that may tend to make mesophase in studies of oil hydrotreating. These findings may be a guide to the reduction in level of certain species in a donor solvent, if proper separation procedures can be devised. Trials of donor-solvent liquefaction of bituminous coals with additions of dried, fine subbituminous coal or lignite may be worthwhile, with and without additions of ferrous sulfate.

Workers on mesophase formation in donor-solvent liquefaction should follow a Japanese technique for the manufacture of metallurgical coke from a wider range of coal rank than was previously suitable for this purpose. In this procedure, a petroleum pitch of special characteristics is added to a blend of coals to be coked. The pitch is such that it penetrates the coals and loses its identity as the blend is heated. Its presence greatly widens the range of temperature during which the viscosity of the pitch and coals remains low. The result is the growth of mesophase domains of the desired large size. Suitable pitches are rich in large, relatively flat aromatic species. Marsh⁸ found that decacyclene, an extreme example of such a species, is the best depolymerizer of coal among those studied. Some solvent-refined coals are suitable

for use as a pitch in the new Japanese procedures for metallurgical coke-making. Hydrogenated SRCs tend to be better.

It is evident that studies of blends of coals and pitch for coke-making may cast some light upon the chemical details that tend to make a good physical solvent for coals. Such information may prove especially important for coals of low rank that are difficult to depolymerize. There is a suspicion that a species ideally suited for the new Japanese coke-making procedures may have a strong tendency for mesophase formation from depolymerized coal and donor solvent containing the species. Compromises with this tendency or the design of a donor solvent based on knowledge of the kinetics of mesophase formation may prove necessary. It seems that measures which tend to lower the temperature of donor-solvent liquefaction also tend to reduce problems arising from the appearance of mesophase.

Workers at Penn State and Exxon have elucidated the formation of calcium carbonate in donor-solvent liquefaction of coals containing high levels of exchangeable calcium ion that is presumably bound in the coals with humic acids.

In electron microprobe traverses of sections of used catalyst pellets, Stanulonis et al.¹² found both titanium and silicon deposits in the interior of the pellets. An interpretation of this finding is that metal organic species containing titanium and silicon had entered the catalyst pores. This interpretation is supported by Kang and Johanson³ who found 750 parts per million of titanium in the asphaltols of an H-Coal liquefaction product from Illinois No. 6 bituminous coal. They³ also found an accumulation of 5.1% titanium in the catalyst after it had been freed of oil. The accumulation was ascribed to deactivation of the catalyst in operations on the Illinois coal.³ It is interesting to note that the catalyst used in treating Wyodak subbituminous coal accumulated negligible titanium, although the ash of both the Illinois and Wyoming coals contained about 1% titanium.

Coleman et al.¹³ have conducted extensive examinations for metals in chromatographic fractions of a number of SRCs; they found a rich variety of metals in a wide range of fractions. The presence of mineral species in the fractions is exceedingly improbable. These results are expected in the light of Ribbe's¹⁴ use of an ion microprobe mass analyzer to detect a variety of metals in the organic portion of West Virginia and Illinois coals. Other authors¹⁵⁻¹⁷ have used the electron microprobe to analyze for trace elements in various petrographic species in coals and have confirmed the presence of metals in macerals. Dreher et al.¹⁸ give data on trace elements in donor-solvent liquefaction residues. An important variable in coal liquefaction is the phenolic content of matter that

reaches hydrotreating.¹⁰ Iron phenolates are reduced when they are hydrotreated. They leave an iron residue that may be identified only after extensive operation. Iron phenolates are highly corrosive, and German engineers learned the importance of keeping a liquid containing these species hot and moving in equipment of low inventory until its phenolic content was reduced. In view of these¹⁰ observations, identification¹³ of high levels of iron in chromatographed fractions of SRCs, especially an SRC from Wyodak coal, may be significant. Also of interest is the report to FERWG by operators of the Fort Lewis, Washington, SRC pilot plant that they had experienced bad corrosion at certain trays of their wash solvent fractionating column.

2.3.2 Research Recommendations

(a) Careful examinations should be made of liquefaction residues from pilot-scale reactors, preferably in several laboratories and by using a number of examination techniques, such as microscopic studies of polished sections of residues in reflected polarized light, chemical analyses by electron and ion microprobes, and determinations of H/C atomic ratios in identifiable organic phases.

(b) Research is needed on the efficacy of various measures to suppress the development of large domains of mesophase. These measures include the addition of "dirt" and the increase in level of heavy solvent species that act as effective hydrogen shuttles.

(c) Analyses should be performed of fresh, quenched samples from pilot plants before regressive reactions have occurred.

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2. 4 Separation Technologies and Coking

In the gasification of coal, all organic material is decomposed and readily separated from the inorganic ash or slag. On the other hand, in the hydrogenation of coal, the objective is usually the production of gaseous or liquid hydrocarbons, which may include very heavy, nondistillable liquids. Depending on the severity of operation, the pattern of products may favor lighter or heavier fractions, but in all cases a bottom fraction will be produced which is not distillable or vaporizable under process or under vacuum conditions.

The "hydroresidue" contains the mineral constituents of the original coals which are changed in composition by the hydrogenation process and also the solid carbon parts of the organic coal molecule remaining after hydrogenation. Since all currently tested hydrogenation processes operate in the liquid phase, these two types of solids are recovered in the form of a slurry, the liquid phase of which represents the heavy, non-distillable, asphaltene-rich bottom fraction of the hydrogenated coal.

The need to withdraw this slurry as a liquid sets an upper limit on the solids concentration, usually around 40%. The ash content is a function of the original ash in the coal and the depth of conversion during hydrogenation.

In the original version of coal-hydrogenation processes (prior to WWII), emphasis was placed on complete conversion to distillables. The coal was very extensively cleaned (down to 3-4% of ash) and process conditions were severe (4000 to 10,000 psi). The total amount of hydroresidue was thus minimized (~10%) and the work-up of this stream, while very cumbersome, was not critical (the amounts were too small to serve as a source of hydrogen). In the new versions of hydrogenation that are now under development, the emphasis has been placed on lowering the severity of the process, with the result that the yield of hydroresidue has increased several fold (it is now from 30 to 50%). As a consequence, the method of work-up and the proper utilization of the residue are of critical importance.

The main goal has been the production of the hydrogen that is required for the overall process; a secondary goal has been the recovery of additional liquids, particularly from hydrogenation which yields a large residue. As a result, two unit operations dominate current efforts. These are liquid/solid separation to recover ash-free or low-ash, non-distillable, liquid products; and gasification of the total hydroresidue slurry or of the solids recovered from the above liquid/solid separation.

To these processes must be added the use of coking (or thermal cracking) in lieu of, or in addition to, liquid/solid separation and finally

consideration must be given to the type of gasifier used to convert residue to H_2 . In the case of fixed gasifiers, the solids must have a minimum size; thus, agglomeration may be required. The attached Fig. 2.4-1 suggests an overall taxonomy of various processing schemes.

2.4.1 Separation Technologies

Solids separation by filtration is attractive for coal-liquefaction processes that produce heavy products since it maximizes the recovery of the product. No other procedure recovers as much liquid as filtration. However, there remain numerous technical problems that must be resolved before satisfactory operation can be achieved. At the Tacoma SRC-I plant, two rotary precoat filters with 40 sq ft and 80 sq ft surfaces, respectively, were utilized in early operations. This procedure involved difficult maintenance problems that led to frequent shut-downs because of mechanical failures and required operational changes. Approximately 3000 tons of product, containing on the average about 0.5 weight percent of ash (with some ash having 0.1-0.2 weight percent in ash), were made in one year. The average production was only 250 tons per month in a plant which had the capability of handling 30 tons/day of solid. The problem of removing filter cake from such a device was not satisfactorily resolved at Tacoma. Process solvent was used to re-slurry the filter cake and remove it from the filter drum. This slurry was then passed to a rotary kiln where nearly all of the solvent was recovered by distillation. Carbonization in the kiln was a troublesome problem.

More successful operations on a small pilot-plant scale were achieved at Wilsonville with a Funda horizontal leaf machine. The leaves have a diameter of about 24 inches. The original machine had a 50 sq ft area, which was later expanded to 100 sq ft by adding additional leaves to a lengthened shell. This operation was reliable and output was no longer limited by filter operation. Dry cake could be produced when the filtration step was followed by a cake-washing step and a vacuum drying step, which was utilized to remove the wash solvent from the cake. The leaves were rotated at about four hundred rpm for a few moments at the end of each cycle. The dry cake was flung from the leaf to the outer wall of the vessel. It dropped from there to the bottom of the vessel for removal from the system. More recently, attempts have been made to operate the plant with a vertical leaf U.S. Filter. However, severe developmental problems have not yet allowed reliable mechanical operation. Understanding of filtration has not been achieved and scale-up of filters to the commercially required 1000-5000 sq ft range is doubtful.

It is of some historical significance that the original development of the filtration step involved the use of ceramic thimbles, assembled in sets,

Fig. 2.4-1 Taxonomy of processing of hydrogenation residues in the production of liquids and of hydrogen. In principle, residues (solid or liquid) may be burned to produce energy as an alternate to gasification.

which were employed in a 100 ton per day pilot plant in connection with coal extraction (Pott-Broche process). This system has recently been reactivated and reasonably successful operation has been achieved with SRC-I effluent from the Wilsonville pilot plant. Also of historical significance is the fact that all nine commercial German hydroplants used centrifuges for separations but that no successful effort to pursue this development has been included in the present DOE program.

Other solids-separation methods (centrifuges, hydroclones) have been used. Recent work on filters of various designs has been disappointing because mechanical difficulties were encountered and low filtration rates achieved (less than 5 gal/minute/sq ft). The relations between process variables and filter performance are not understood. Research programs now underway at several universities may lead to improved understanding.

Two deashing systems of great interest for SRC-I technology are currently being tested. These are the Kerr-McGee solvent deashing unit at Wilsonville and the Lummus deashing unit at Tacoma. The Kerr-McGee system uses low boiling aromatic solvents at operating conditions above the critical temperatures and pressures of the solvents to extract soluble components from the products. The non-soluble components are discharged as a solid from the extraction vessel. The solvent is flashed from the product and returned. The Lummus deashing process uses a paraffinic, low boiling hydrocarbon that precipitates, agglomerates and throws out of solution solids that are suspended in the product. The solvent in this type of application is referred to as an "anti-solvent." Paraffinic solvents that boil at 200-300°C were used. Workers at Dow Chemical have applied a similar technique in their process. A virtue of the Lummus and Dow separation techniques is the fact that the ash is let down as a pumpable, viscous liquid that contains about 40% ash which can be transferred quite readily to a gasification process.

With both the Kerr-McGee and Lummus methods, reasonably successful mechanical operations were achieved during 1979. The critical solvent deashing technology at Wilsonville has also been utilized to break down the recovered product into light and heavy fractions, as well as to reject material with high ash content. The solids-containing stream emanating from such an operation contains about 50-65% ash and unconverted coal. After flashing is used to recover the deashing solvent, a finely divided powdered solid is formed. Process investigations have focused mainly on the relations between liquefaction operating conditions and the thermal reactions occurring between the liquefaction system and the deashing step.

It has been demonstrated that recoveries as high as 83% of the SRC can be achieved in the feed to the Kerr-McGee unit. Multi-stage operations have proven to be reliable and few mechanical problems remain. Scale-up of the Kerr McGee technology should be considered after completion of the work at Wilsonville in 1980. Operation of the Lummus unit at the Tacoma pilot plant in 1979 achieved a reasonable level of success with SRC recovery levels in the 65-70% range when operating on an SRC-I product derived from a Kentucky coal. The limitations on product recovery from a Lummus unit are largely dependent on the viscosity of the underflow stream from the clean-product vacuum tower. This material is used as a source of gasification feedstock, which must flow for removal from the vacuum tower and subsequent downstream handling. During 1981, H-Coal process operations in the fuel-oil mode at Catlettsburg will use a much larger Lummus unit at the 600 ton/day scale. This operation will benefit from the experience gained at the Tacoma pilot plant; contacting and materials problems should be resolved during 1981 at the H-Coal site.

The Lummus, Dow, and Kerr-McGee separation technologies are proprietary. Thus, internal studies of contractors, operating procedures, techniques, and other information, are considered to be confidential. For this reason, it may be difficult to implement significant, separate fundamental studies, especially since existing programs are not readily separated from engineering requirements. In the area of separation technologies, only an augmented program to define the mechanisms and efficiencies of filtration processes appears to be warranted.

2.4.2 Coking

Coking will be the more attractive the more "liquid" phase is contained in the hydro-residue (i.e., the more H_2 has been added during hydrogenation). Coking will normally be carried out at thermal cracking temperatures that maximize the recovery of lower molecular weight (distillate) liquids (900-1000°F). Three types of coking operations may be considered.

A. Fixed Bed Coker

Delayed coking is a large commercial operation. It is possible to modify process conditions to accommodate hydroresidues as feed. In view of high ash content, the resulting coke (obtained by hydraulic de-coking) may be of a size-consist that is sufficiently coarse to allow its use in fixed-bed gasification systems. Several U.S. laboratories have delayed installation of pilot facilities to determine the feasibility of using this concept,

B. Fluidized-Bed Coker

Residues were coked in fluidized beds in the Cresap Pilot Plant programs of 1969/70 by Consolidation Coal and again in 1978 by the Fluor Corporation. A draft-tube system was used to accommodate the caking properties of the residue. This consisted of a simple airblown atmospheric operation, which yielded the theoretically available coker distillate.

The fluid-bed coking principle will be explored in the Flexicoking process of Exxon as part of the EDS pilot-plant program. Fluid-bed coking yields finely divided, solid char.

Flash carbonization may be suitable for handling the hydroresidue with high liquid recovery and its application to residue processing should be considered.

C. Other Hydro-Residue Cokers

The ten commercial German hydrogenation plants operating in the 1935-1945 period all used an externally fired rotating kiln that was filled with steel balls to carbonize the final residue which was obtained by centrifuging the non-vaporizable sludge. In German practice, the residue represented only a rather minor disposal problem since some 90% of the MAF coal was converted to a vaporizable product. The capacity of these coking units was, therefore, small.

Since gasification in fixed-bed gasifier represents by far the largest fraction of gasification capacity, it is of interest to use a hydro-residue coker which yields the solid coke in a sufficiently large size for use in these fixed-bed systems. One-quarter inch or larger particles are adequate and, given the low bed height of the gasifiers (~15 ft), there is no great demand for particle strength. Usable particles are obtained either by adding an agglomeration (briquetting) step to treat the finely divided coke obtained in a fluid-bed carbonizer or by combining the coking operation with the agglomeration step by pelleting at coking temperatures. This hot pelletizing of hydro-residue slurries was developed by Conoco at the 10-15 ton per day scale.

We are not aware of research needs in the area of coke formation.

2.5 Generation of Hydrogen and Fuel Gas from Residues*

Direct conversions of coal to liquid produces high boiling liquid or solid slurries that are carbonaceous and contain ash, as well as relatively large amounts of sulfur and nitrogen compounds. These products may be utilized for the generation of process heat or for the production of hydrogen. The slurries may contain 25-40% ash. Depending on the separation technology used, the residual product stream may be either a high melting point liquid with high viscosity or a solid. Liquids that can be pumped are recovered in the H-Coal (synthetic crude mode), Exxon EDS, and SRC II processes and represent 20-40 weight percent of the original coal. The slurries may be disposed of for gasification, combustion, and coking (which is then followed by coke combustion or gasification).

2.5.1 Hydrogen-Generation Technologies

In an integrated coal-liquefaction plant, hydrogen must be generated either from the coal itself or from products of the coal-liquefaction reaction (see Fig. 2.5-1). The best hydrogen-generation technology must be sought in connection with an evaluation of methods for supplying electricity, steam and fuel gas to the liquefaction plant.

Table 2.5-1 shows feedstocks for gasification processes that supply hydrogen or fuel gas. Steam-methane reforming was considered to be the preferred method in early liquefaction plant designs for generating hydrogen because it is a developed commercial process. However, the potential availability of a market for the methane produced in the liquefaction process, as well as the high fuel requirements for the reforming furnace, now make this approach less desirable.

Gasification of vacuum-bottoms residues has become an economically preferred method for producing hydrogen from pumpable residues. However, it is not always possible to balance production with need. If residue production is too low, which is rarely the case, additional coal must be utilized. On the other hand, if vacuum-bottoms production is higher than the level required to balance the plant, methane must be exported as a product or utilized to generate power.

*The material presented in this Section 2.5 has been abstracted from lectures prepared by R. H. Wolk of the Electric Power Research Institute (1979). For an extensive discussion of coal-gasification technologies, we refer to the first FERWG report: "Assessment of Long-Term Research Needs for Coal-Gasification Technologies," Mitre Technical Report MTR-79-W00160, The Mitre Corporation, Metrek Division, 1820 Dolley Madison Boulevard, McLean, Virginia 22102, April 1979. This report is hereafter referred to as I.

Fig. 2.5-1 Schematic diagram of a representative liquefaction plant.

Table 2.5-1. A partial listing of hydrogen-production processes .

From coal: Lurgi, Winkler, Texaco, Shell-Koppers, Koppers-Totzek, Saarberg-Otto processes.

From pumpable residues: Texaco, Shell, Flexicoking (for fuel gas only) processes.

From non-pumpable residues: Koppers-Totzek, Water-Slurry Texaco, Shell-Koppers processes.

From gases: steam-methane reforming, partial oxidation.

The dry-bottom Lurgi gasifier may be used with noncaking and with some of the moderately caking coals to produce a mixture rich in CO and hydrogen, which can be subsequently shifted to hydrogen. A convenient method for disposing of the tars that are always produced in the plant is to pass them through the liquefaction or through a hydrogenation reactor. A coal-water slurry fed to a Texaco partial oxidation gasifier is also a source of CO-H₂ mixtures. Entrained-flow gasifiers using dry-coal feeds may also be used for this purpose; these include Koppers-Totzek gasifiers (which have been operating commercially for years at atmospheric pressure) and Shell-Koppers gasifiers (which are now operating at a scale of 150 tons per day at about 20 atmospheres).

If all of the methane produced (representing 5-8% of MAF coal) is to be consumed within the plant, it is conveniently steam-reformed to provide hydrogen for the liquefaction plant. Gasification of pumpable liquefaction residues may be carried out in the Texaco or Shell partial oxidation units. Many commercial units have been licensed by both Shell and Texaco for processing residual oils. A program to verify successful partial oxidation of coal-liquefaction residues merits support.

Liquefaction operations, which produce filter cake as residual product, may use a Koppers-Totzek gasifier. If a Kerr-McGee critical donor-solvent deashing unit is utilized as a means of solids separation, then the dry powdery solid emanating from this process may be fed either to a Koppers-Totzek unit, to a pressurized Shell-Koppers system, or alternately briquetted and fed to a Lurgi unit. In the EDS unit, the Flexicoking process (which consists of a sequential fluid coker and gasifier) is used to recover liquid products from a vacuum-bottoms residue, as well as to generate some coke which is then gasified with air to generate fuel gas.

The optimum configuration for hydrogen generation depends on the coals and the liquefaction process. The current status of gasification technologies is summarized in Table 2.5-2; corresponding gas compositions are given in Table 2.5-3.

A. Status of Technologies

The Texaco partial oxidation process is often shown as the preferred system for the gasification of vacuum-bottoms residues (see I for details). Residues from the H-Coal, SRC-II and Exxon projects have been gasified and are identified in Table 2.5-4. A long-term (2 week) run was performed on SRC-II vacuum bottoms (1979). This material, which was obtained from the Tacoma SRC-II pilot plant, has a cut point of about 850°F and is somewhat more fluid than samples obtained at 900-1000°F cut points in the smaller scale H-Coal (3 TPD) and Exxon (1 TPD) process-development units.

Table 2.5-2. Gasification process status (1979).

Licensors	Type	Oxidant	Pressure, psi	Status
Lurgi	dry-bottom, moving bed	oxygen	400	commercial for non-caking, sized coals
	slagging, bottom-moving bed	oxygen	400	300 TPD at Westfield, Scotland
Texaco	entrained, water slurry	oxygen	350	150 TPD, operational at Oberhausen, Germany
		oxygen	350	150 TPD, under construction at Muscle Shoals, Alabama
		air	350	150 TPD, operational on lignite at Plaquemine, Louisiana
Koppers-Totzek	entrained	oxygen	atmospheric pressure	commercial for powdered coal
Shell-Koppers	entrained	oxygen	350	150 TPD, operational at Harburg, Germany
Winkler	fluidized-bed	oxygen	atmospheric pressure	commercial

Table 2.5-3. Representative gas compositions obtained in the gasification step.

Process	Feed	% H ₂	% CO	% CO ₂	% CH ₄
Texaco (coal gasification)	coal-water slurry	30-40	40-50	15-20	0.1
Texaco (residue gasification)	molten residue	34-39	55-59	5-6	0.1
Koppers-Totzek	pulverized coal	27-32	54-57	10-14	0.1
Shell-Koppers	pulverized coal	25-30	60-65	2-3	0.1
Winkler	granular coal	36	46	14	2
Lurgi	sized coal	39	16-20	30	10

Table 2. 5-4. Gas compositions obtained for liquefaction residues in the Texaco partial oxidation process at the 12 TPD scale. All tests were run at 350 psig for 6-12 hours.

Source of Feedstock	% H ₂	% CO	% CO ₂
H-Coal vacuum bottoms	39	55	5.5
SRC-II vacuum bottoms	34	59	5.8
Exxon donor solvent bottoms	38	52	8.8
SRC-I vacuum bottoms	37	58	4.1
SRC-I filter cake (water slurry)	31	41	26

Coal-liquefaction vacuum residues with high solids content and high average boiling point are thermally unstable. Viscosity increases of several fold occur during long-term, high-temperature storage (500-600°F) of vacuum residues. Since sufficient surge capacity must be built into an actual system to assure the reliability of operation of the gasifier, care must be taken to design the system properly. The sizing and actual temperature level of the surge system must be carefully specified so that the vacuum bottoms delivered to the burner tip have appropriate viscosities. Additional problem areas involve burner-tip and refractory service lives. The burner-tip life may be limited by erosion because of the high concentration of finely divided and erosive solids in the feed material. Probably of much greater significance, however, is the potential for attack of refractory in the vessel. The rate of attack is a function of both the slagging chemistry of the coal-liquefaction residue and of the temperature of the refractory surfaces. Different refractories will be required for different coals.

Useful information on coal-water gasification in the Texaco process will be obtained during the next few years from operation of three 150 TPD gasifiers. The first unit brought on stream is located in Oberhausen, Germany, at a Ruhrchemie plant. It is used to gasify a water-coal slurry and to recover heat in a radiant boiler. Fewer details are available on a Dow Chemical unit at Plaquemine, Louisiana, which is believed to be operating as an air-blown system fed by a lignite-water slurry. A third unit is being built by TVA at Muscle Shoals, Alabama; this unit will be used to obtain data on a number of coals that TVA is interested in gasifying to produce CO-H₂ mixtures, which are to be fed to an ammonia plant. The TVA unit will be equipped with a recycle-gas quench to cool reactor effluents. When manufacturing hydrogen or fuel gas for a liquefaction plant, it is not necessary to use a waste-heat boiler to optimize heat recovery. Waste-heat boiler design remains as a large developmental task. Typical flowsheets are given in Figs. 2.5-2 and 2.5-3 for the direct-quench and gas-cooler modes of operation.

A major problem that was identified during the early work at Oberhausen involved temperature measurements. Thermocouple lives were extremely short because of destruction of protective coverings by slag and attack on Pt/Rh wires by hydrogen. Service lives have now been increased to 300 hours by employing different materials and altering the location of the couples. Development of the Texaco gasification system beyond the 150 TPD scale is scheduled to occur with the 6000 TPD SRC-II demonstration plant that is now being designed. The design-pressure level of the gasifier will be 600-800 psig; no experimental work has as yet been carried out at this pressure level on residues since all previous work (at the Montebello, California, facility) on residues was

Fig. 2.5-2 The Texaco coal-gasification process operating in the gas-cooler mode.

Fig. 2.5-3 The Texaco coal-gasification process operating in the direct quench mode.

limited to a maximum pressure of 400 psig. Some higher pressure operations were performed during 1979.

A process analogous to that of Texaco has been developed for residual oil gasification by Shell. There are no open literature releases to show that extensive work has been done on liquefaction residues.

B. Steam-Methane Reforming

Steam-methane reforming is a commercially available technology for the production of hydrogen. However, it is a large consumer of fuel. Designs developed by Exxon feed the process-derived methane through the catalyst tubes while firing these tubes with low-BTU gas produced from residual materials by Flexicoking (cf. I). The use of low-BTU gases for this service increases the volume of the fire boxes needed for combustion and also requires a large fuel-gas distribution system. It is unlikely that methane will be used in a steam-methane reformer if it can be sold as a product from a liquefaction plant at a value close to the energy value of the liquids. Recent economic studies prepared by Exxon indicate that the steam-methane reforming route is expensive.

C. Shell-Koppers Process

Shell and Krupp-Koppers began development of a dry, pressurized, pulverized coal, slagging, entrained gasifier in 1974. The key technical problem that had to be overcome in this development was finding means for continuously injecting dry powdered coal into the gasification vessel. A 6 TPD pilot plant has been operated at Amsterdam since 1976. This unit was followed by construction of a 150 TPD unit at the Shell-Harburg refinery, which is capable of operation at 20-40 atm. Successful sustained operations have been reported recently. A simplified flow scheme for this process is shown in Fig. 2.5-4.

The ability to feed dry coal reduces the thermal load on the gasifier since a significant amount of water need not be vaporized. The CO_2 level in the gasifier effluent is reduced to about 2 volume percent. The value of this feature is somewhat diminished if the gasifier effluent is to be shifted to produce hydrogen since steam must then be added downstream. Several key advantages have been claimed for the technology. These include a number of proprietary systems such as a coal-design system based on lock hoppers that allows continuous operation, and a system of cyclones and scrubbers to remove particulates from the raw gas without the use of scrubbing water.

Fig. 2.5-4 A simplified flow diagram for the Shell-Koppers coal-gasification process.

There are two specific uses for this type of gasifier which should allow significant improvements in process economics over a conventional, atmospheric Koppers-Totzek gasifier. Gasification of powdery ash concentrate from the Kerr McGee critical solvent deashing process may be an appropriate use for the Shell-Koppers process. Ash levels in this material are on the order of 40 weight percent.

A second application of interest is the feeding of lignite or sub-bituminous coals, without the use of slurrying water (as in a Texaco process) to produce synthesis gas. These coals contain 30-50 weight percent of inherent moisture, which cannot be permanently removed by drying if the drying step is followed by slurrying in water. This problem may prove to be significant in projects manufacturing methanol from low-rank coal.

D. The Koppers-Totzek Gasifier

The Koppers-Totzek gasification process is an atmospheric, oxygen-blown, system which has been in commercial use at many locations in the world in plants used for ammonia and methanol production. It is capable of gasifying such materials as filter cakes and Kerr-McGee residues, which contain significant carbon contents. The use of this gasification step allows recovery of the BTU contents in low-carbon materials through conversion to CO-H₂ mixtures. The Koppers-Totzek process operates at atmospheric pressure. As the result, the cost of the gasification system in a liquefaction plant is quite high because of the compression costs involved in raising the product gas from atmospheric pressure to the liquefaction pressures. It is much more economical to use pressurized gasification operating at the 400 or, preferably, at the 800 psig level.

E. Lurgi Gasification

Lurgi moving-bed, pressurized, oxygen-blown gasification, with either a dry or a slagging bottom, may be of some use in liquefaction processes where liquid yields are very high and gas and residue yields are low. This yield mix makes the plant short of fuel and/or hydrogen. Gasification of sized coals can be used to meet these needs. Lurgi technology is attractive since it has been used on commercial scales for many years at a large number of facilities.

Recent successful operation of the slagging-bottom Lurgi unit by the British Gas Corporation at Westfield, Scotland, on mildly caking U.S. coals containing some fines may expand the capability of the technology. The higher throughputs may make this process economically competitive for hydrogen generation in liquefaction plants.

2.5.2 Recommended Fundamental Studies

In contrast to existing programs on coal liquefaction, there is no significant effort on utilizing the 20-50% of the product that is in the form of residues (boiling at about 450°C). Attention to obtaining test data in 1-10 TPD gasification equipment and further scale up to 150 TPD tests of long duration in pilot-plant equipment is of high priority. Many experts working on coal liquefaction believe that the utilization of residues is likely to be a limiting element in establishing commercial synthetic oil plants.

Fundamental programs relating to the gasification of solid and liquid residues are similar to those required for coal gasification (cf. I). Here, we emphasize two important areas of research.

A. Combustion

There has been practically no work done on utilizing ash-containing residues in combustion equipment. However, limited studies have been performed on the use of residues to provide process heat for heating steam-reformer tubes (a single ceramic tube was tested), for a hybrid boiler arrangement (Exxon), and for fluidized-bed combustion. These schemes are attractive in an integrated process because of the use that is made of low-quality products. Research programs to develop utilization methods for residues are justified.

B. Coking

Delayed coking and low-temperature carbonization of residues are not being considered seriously. The Exxon EDS process involves development of the Flexicoker for disposing of residues to fuel gas. Gases with low heating values are derived by air blowing the coke produced in a fluid coker. A small amount of liquids is distilled from the vacuum-residue feed. In work done on a relatively small scale, workers at Exxon have shown that the ash in the feed can produce slag. Remaining uncertainties suggest that the Flexicoking process should be tested in a 70 TPD pilot plant.

2.6 Instrumentation and Control

All of the direct coal-liquefaction processes are being developed with inadequate monitoring and control instrumentation. This problem is well recognized by project engineers, plant managers, and DOE program monitors.¹ In particular, improved instrumentation is required for the following applications: slurry flow-rate measurements, especially at elevated temperatures and pressures; analyses of mixture compositions of recycled slurries; measurements of fluid and slurry levels and interfaces; the design and operation of reliable letdown valves in high-pressure, heated slurry lines; accurate temperature measurements and temperature controls (in heated slurry lines and in such critical components as the dissolver) over a wide range of pressures; viscosity and rheometry measurements in slurry lines over wide ranges of temperatures and pressures; early detection of agglomerations to prevent plugging of line flows; on-line analyses of coal-feed size distributions and flow rates.

In spite of clearly defined needs in the instrumentation and controls (I&C) areas, program managers generally believe that the existing recognized deficiencies will not prevent successful operation of pilot and demonstration plants, although preferred designs generally include generous allowances for redundant or replaceable components that are known to have short service lives (e.g., let-down valves, slurry pumps).

2.6.1 I&C for the SRC-II Process

A simplified block-flow diagram for the SRC-II process has been shown in Fig. 1.2-1; more detailed information is contained in Section 1 of Appendix C. The principal instrumentation problems encountered in the SRC-II process relate to the dissolver area and are traceable to the high erosion produced by high-temperature slurry streams containing ash; pressure and, to a lesser extent, temperature gradients produce rapid changes in slurry density which are not accurately predictable because of inadequate characterization of the physico-chemical properties of the slurry.

The following types of measurement have been judged¹ to be desirable but generally "beyond current technology": onstream composition analyses of the percentages of solids, on-line measurements of moisture contents of coals (for which infrared and microwave techniques have been suggested), pH measurements at 1990 psig at dissolver temperatures (~800-900°F), rapid analyses of coal BTU contents, slurry viscosities at elevated temperatures, slurry-level measurements at ~2000 psig and ~800°F (capacitance probes and γ -ray detectors may be suitable), temperature measurements in the dissolver with high spatial resolution and under conditions of erosion, caking and coking.

Pressure relief devices in slurry flows have been identified as a special problem because of possible coking at the inlets (the use of rupture discs under the valves has been suggested). It is expected that the rapid expansion of slurry fluids will severely damage relief valves.

Success has been claimed¹ for slurry-flow meters using a stellite quadrant edged orifice plane with downward flow. Other slurry flow meters that will be tested include an elbow meter, a segmental wedge, a thermal flow meter, target meter, venturi tube, and a mass-flow meter utilizing Coriolis acceleration.

The let-down system for the SRC-II demonstration plant is a three-stage system that may be operated with only two stages. The best experience at Ft. Lewis for the let-down valve has involved the use of a Fisher angle valve with tungsten carbide trim that has yielded a maximum service life of about two months. It is likely that the problem with let-down valves will be alleviated when the small ($\sim 1/8$ " diameter) openings in the pilot plant are scaled up to 1.5-2.0" diameter in the demonstration plant.

It has been suggested to use the actual horsepower employed in driving the pump or mixer as an indicator of slurry density at a particular temperature.

A preproposal has been prepared at the Argonne National Laboratory² for development of instrumentation needed for the SRC-II demonstration plant. The following types of instruments are included:^{2,3} acoustic (e.g., Doppler) flowmeters,⁴ capacitive⁵ and nuclear techniques for flow measurements; capacitive and acoustic level sensors; on-line composition analyses using neutron-induced gamma-ray spectrometry, optical techniques, and acoustic measurements.

2.6.2 FERWG Recommendations on I&C

The need for improved I&C is a recognized problem that is being adequately attacked by industrial groups and at the Argonne National Laboratory (ANL). Required process instrumentations and controls should become available in usable form soon after the need for these devices is recognized to be of critical importance for successful plant operation. We support current initiatives as minimum requirements in meeting urgent I&C needs.

It is apparent that long-term efficacy of I&C operations requires also sustained support of longer term studies that are not directly tied to operational needs. For this reason, we recommend that funds for

instrument development be made available to university and other groups for studies in which broad areas of application are identified, including measurements of slurry flows, on-line viscosity determinations, temperature measurements in multi-phase flow systems, etc.

REFERENCES

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2.7 Scaling and Modeling of Liquefaction Units

Significant scaling and modeling issues for coal-liquefaction processes are associated with the slurry preheater and with the liquefaction- and downstream-reactors. These units support three-phase flows accompanied by heat and mass transfer and by chemical reactions. In this section, it is assumed that important fundamental questions associated with determinations of expressions describing the chemical kinetics are adequately addressed (cf. Section 2.1). Here, we focus on the physical processes involved in scaling and modeling.

2.7.1 Existing Technology

Existing techniques applicable to the scaling and modeling of liquefaction units involve four interrelated levels of activity.

A. Thermophysical properties are needed. The properties of the pure components are readily correlated and may be predicted, in some cases, by using existing knowledge and techniques. The properties of mixtures (density, viscosity of Newtonian fluids, and vapor-liquid equilibrium for nonpolar, lower molecular weight compounds) represent no significant problems.¹ Accurate values are also available for the chemical equilibrium constants of the simpler gas-phase reactions.

B. The phenomenological behavior and rate processes associated with single-phase flows in simpler geometries (e.g., pipes and tubes, packed beds, stirred tanks, etc.) are adequately described by introducing the appropriate transport phenomena into the governing equations if property data are available. This procedure yields velocity and shear-stress profiles, film coefficients for heat and mass transfer, pressure drops, etc. Two-phase, gas-liquid flow phenomena have also been adequately accounted for in a number of situations. An important exception must be made to this last statement because of the need, in almost every case, to develop empirically applicable kinetic expressions to describe the rates of chemical reactions in such a manner as to account for observed data.

C. Process-unit simulation is accomplished by performing a synthesis of the mathematical expressions for the applicable phenomenological behavior, along with the kinetic expressions (in the case of reactors), into a mathematical model which is deemed to be capable of predicting the performance of the particular unit operation. Numerous useful numerical techniques have been developed for the solution of the simultaneous algebraic equations or the integration of the simultaneous ordinary or partial differential equations that govern the flows.

D. Flowsheet simulation (COPE, Flowtran, ASPEN) has come into common use during recent years. This type of simulation is used to perform heat and material balances for integrated processes, most of which include a number of recycle streams. These programs provide means for rapid evaluation of the impact on the overall process of changes in the design or operating conditions of a single process unit. They represent one example of a broader class of techniques that is usually referred to as computer-aided design. Other examples include programs which synthesize "optimal" heat exchanger networks and separation schemes or perform "second law" analyses on process flowsheets.

2.7.2 Importance to Liquefaction

The development of accurate or adequate models for the various units involved in liquefaction will decrease the time required for the scale-up of unit sizes. Furthermore, models also provide an opportunity to manipulate design variables and options in such a manner that a pioneer plant will be closer to an optimal design.

The basic philosophy of economical scale-up involves determination at each stage of critical uncertainties. These questions are resolved at the smallest possible scale and under the least severe conditions that will still give an answer that can be used with confidence. For example, questions on reaction chemistry are usually answered on the bench scale in glassware, tubing bombs or thermobalance reactors. Considerations of conversion in continuous reactors are typically addressed in a small pilot-scale feasibility study involving only the reactor. The impacts on the process of factors such as side reactions, trace components in recycle streams, and process control are generally studied in integrated pilot plants or process-development units. Data on equipment performance and demonstration of long-term operability are obtained in a large pilot plant. Finally, removal of remaining critical problems and optimization of the commercial process will usually result from operation of the pioneer plant itself. The availability of good mathematical models, based on the use of fundamental data, will usually shorten the required test time at each stage and may eventually lead to a pioneer-plant design that is acceptably close to optimal.

2.7.3 State of Knowledge

The current state of knowledge in reactor scale up has been summarized by Shah.²

2.7.4 Long-Term Research Needs

In order to scale up and model coal-liquefaction process units, research is needed to identify, measure, and correlate the important design parameters involved in multiphase coal conversion. Among the important design parameters are knowledge of flow regimes and flow uniformity, pressure drops, holdups of various phases, heat and mass transfer between phase combinations, intraparticle heat and mass transfer, and heat transfer to vessel walls and surfaces. Overall process modeling is facilitated by using advanced, computer-aided design tools for flow-sheet simulation and process synthesis. These will increase the probability of attaining an optimal design more quickly and then will also help in identifying those specific process units which have the greatest impact on overall design and for which more detailed development work is required.

2.7.5 Opportunities for Research

A. Research opportunities for determination and correlation of thermophysical properties include the following:

- (a) Development of vapor-liquid equilibrium correlations applicable to heavy, more aromatic and/or polar coal-liquid components.
- (b) Measurement and correlation of free energies of formation for components encountered in coal-liquefaction processes and the development of expressions for the chemical equilibrium constants of the significant reactions.
- (c) Experimental measurements and development of mixing rules for density, viscosity, heat capacity, thermal conductivity, etc. The final relations should be applicable to the compositions encountered in liquefaction processes.
- (d) Quantification of the behavior of the multiple liquid phases which are encountered (e.g., separation of aromatic asphaltenes from an aliphatic phase).
- (e) Measurements and correlations of enthalpies and free energies associated with phase changes and mixing for the components encountered in coal liquefaction.
- (f) Measurements and correlations of the physical properties of coals and of catalysts that may be used.
- (g) Measurements and correlations of the solubilities of various solid- and gas-phase components in liquids with compositions encountered in liquefaction processes.

B. Opportunities for research in transport phenomena and other rate processes applicable to coal liquefaction include the following:

(a) Evaluations based on appropriate theories (e.g., film theory, penetration theory) of the gas-liquid-solid reaction systems encountered in liquefaction reactors (with both fixed and fluidized solids); determinations of rate processes applicable to slow reactions of a solid (as in thermal coal liquefaction), show reactions of a solid used as a catalyst (as in Fischer-Tropsch synthesis), and reactions of solids present as both catalysts and reactants (as in catalytic coal liquefaction).

(b) Measurements of reaction rates and the development of usable kinetic expressions that are suitable for applications to chemical reactors. This work should apply not only to reactions in the liquefaction unit but also to reactions which take place in the slurry preheater, hydrotreaters, cracking reactors, coking reactors, etc.

(c) Development of correlations for axial and radial dispersion of heat in three-phase systems.

(d) Development of heat-transfer film-coefficient correlations for slurry and three-phase flows in tubes, for use in heaters and in heat-exchanger modeling.

(e) Development of rheological models for non-Newtonian slurries, which account properly for the influences of particle-size distributions and the rheological characteristics of the liquid phase.

C. Opportunities for research on process-unit simulation and techniques applicable to the scale-up of coal-liquefaction processes units include:

(a) Experimental determinations of residence-time distributions (RTDs) in all three phases on laboratory, pilot, and commercial scale vessels, at various flow rates, particle-size combinations, and L/D ratios. These data should be related to various existing or new mixing models in order to determine the best models for applications at various stages of scale-up.

(b) Determinations of the effects on the gas-flow regimes (bubble, slug, mist, etc.) of column diameters in three-phase systems. The effects associated with the design of distributors should also be studied at various scales of operation.

(c) Development of models for three-phase systems in vessels when significant vapor evolution occurs.

(d) Development of improved laboratory reactors which have RTDs that closely resemble large-scale commercial units so that meaningful yield data can be obtained on a small scale.

(e) Development of laboratory reactors and of the corresponding data-reduction techniques to provide applicable kinetic data.

(f) Mathematical modeling and experimental studies on the stability and transient behavior of liquefaction reaction units. Process-control strategies, based on these studies, should also be developed.

D. Research opportunities in computer-aided designs include the following:

(a) Development of data structures and algorithms for handling flowsheet-simulation programs which include proper considerations of the properties of three-phase systems (including solids and their size distributions).

(b) Development of simulation modules which consider the distribution of solid particle sizes (population models).

(c) Development of supervisory modules which will adjust design variables to achieve maximum thermal efficiency while converging the recycle network.

(d) Development of techniques and computer programs to aid in performing practical second law analyses of process flowsheets. These programs need to take into account constraints imposed by temperature limits, start-up requirements, safety considerations, etc.

It is likely that industry-based programs on scale-up and modeling will profit from the coordinated support of university studies on the methodologies that are used for reactor scale-up.

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2.8 Down-Stream Refining of Coal-Derived Liquids

Commercial coal liquefaction projects, particularly those intended to substitute for imported foreign crudes in the domestic transportation fuel market, need to be integrated into the existing domestic transportation and refining systems. The overall economics from coal to marketable products will be the principal basis of decision on location of plants and transportation of intermediate products. Environmental and health concerns and regulations may override otherwise acceptable decisions.

2.8.1 Refining Technology for Coal-Derived Liquids

Current direct coal liquefaction technologies produce substantially different qualities of raw coal oils. All of the coal-derived oils are very different from petroleum crude oils and distillates. Generally, they are too high in aromatic, condensed-ring, and heteroatom concentrations (nitrogen, oxygen, and sulfur) for use in the transportation fuel market without further refining. However, the distillate fractions from raw coal oils can be processed with current petroleum-refining technologies to produce near-specification transportation fuels. We list in Tables 2.8-1 and 2.8-2 examples of jet and diesel fractions produced from H-Coal, Illinois No. 6 (Burning Star) synthetic crude by severe hydrofining. Hydrofining severities and hydrogen consumptions were slightly different in these two pilot-plant studies.

It is known that coal-derived naphtha fractions, particularly after two-stage reforming, produce excellent high-octane gasoline blend stocks. Refining to less aromatic jet and diesel fuels may be more difficult. Products of this quality, particularly if blended with petroleum-derived jet and diesel fuels, should cause few, if any, problems with current engines. However, this result was achieved only at significant cost. For example, the diesel fraction was obtained at a yield of about 90 volume percent from whole H-Coal oil with a hydrogen consumption of about 2200 SCF/bbl, corresponding to a cost of \$6-9/bbl.

The development of engines that are more tolerant to fuels with high aromatic contents and with high heating values will reduce the refining costs for these products. As increasingly large fractions of the transportation-fuel market are being supplied by direct coal liquefaction, the option of redesigned engines should be considered in an overall economic evaluation (compare Section 8.2 in Appendix C). However, at the present time, the most direct and simplest route is to move these oils to market as a partial substitute for petroleum, especially by using them in existing petroleum refineries.

The uniquely aromatic nature of coal liquids opens up two other diverse areas for research needs. Firstly, a very broad spectrum of

Table 2.8-1. Jet fuel produced at Chevron Corp. from H-Coal synthetic crude derived from Illinois No. 6 (Burning Star) coal .

Property	Jet A specification (ASTM D 1655-78)	Properties of the 250°F product from severely hydrofined Illinois H-Coal oil
gravity, °API	37-51	36.3
smoke point, mm	>20	23
freeze point, °F	<-40	-53
thermal stability, jet fuel thermal oxidation test at 260°C	No. 1 or No. 2	No. 1, $\Delta p = 0$
aromatics, liquid volume %	<20	2.7
existent gum, mg/100 ml	< 7	incomplete
corrosion on a copper strip (2 hours at 212°F)	No. 1	No. 1
end point, ASTM #D86	<572	589
flash point, °F	>100	108

Table 2.8-2. Diesel fuel produced at Chevron Corp. from H-Coal synthetic crude from Illinois No. 6 (Burning Star) coal.

Property	Diesel fuel specification ASTM D 975-78		Properties of the 250°F product from severely hydrofined Illinois H-Coal oil
	No. 1D	No. 2D	
cetane number	> 40	> 40	42.5
cloud point	varies	varies	50
sulfur, weight percent	<0.5	<0.5	0.001
flash point (Pensky-Martin), °F	>100	>125	116
ash, weight percent	<0.01	<0.01	< 0.002
distillation 90%, °F	< 550	540-640	524
viscosity at 40°C, centistokes	1.3-2.4	1.9-4.1	1.678
viscosity at 100°F, Saybolt universal seconds	< 34.4	32.6-40.1	32.1
Cu-strip corrosion	< No. 3	< No. 3	No. 1
aromatics	-	-	2.7

chemicals can be recovered from various product streams. The heterocyclic nature of numerous compounds makes coal liquids suitable for extractive separations. Very high volumes of BTX can be extracted from the reformat streams. Phenolics are extractable from raw naphtha. Numerous other opportunities exist and await identification. Research will contribute to energy-efficient separation processing for a broad range of chemicals. A second need exists in the areas of health and industrial hygiene effects relating to coal-derived liquids. Broad-based evaluations of raw and upgraded (hydrotreated/extracted) streams are needed to assess short-term and long-term health issues associated with use as chemicals. A major concern is the carcinogenic nature of many high molecular weight polynuclear (polycyclic) aromatics (PNAs). Procedures need to be developed to insure the health of the workers in the industry and limits need to be defined for PNAs in coal-derived products.

The foregoing comments relate to liquids derived from coals by any of several direct hydroliquefaction routes. Indirect routes through gasification and Fischer-Tropsch synthesis (Sasol) or methanol to gasoline conversion (Mobil process) produce very different products. Fischer-Tropsch synthesis products are highly paraffinic and may contain appreciable amounts of chemically combined oxygen but they are essentially free of nitrogen or sulfur. These liquids should present no particular refining problems, other than those associated with high paraffinicity (i. e., high pour point, high cloud point, low octane number, etc.). The products produced in the Mobil M process are reported to be mainly highly aromatic, high-octane naphtha and C₄ and lighter gases. These products should be directly usable in any transportation fuel refinery.

Mention should also be made of other energy uses for coal-derived liquids, especially electric power generation. As substitute fuels for coals in boiler plants, raw coal feeds such as SRC-I should be satisfactory with proper burner design and configuration. The use of lighter, coal-derived distillates as fuels for combined cycle power plants may require changes in turbine design because of the high aromaticity of these fuels. Also, NO_x emissions could prove to be a problem that will require the use of remedial measures.

A. Research recommendations

While refining processes capable of producing conventional fuels from coal-derived oils are available, high hydrogen consumption, poor selectivity and, in some cases, low catalyst activity and life leave room for major improvement. The large industrial capability for development of petroleum-refining processes is a major national resource for the

development of synthetic fuel refining processes. While there is a considerable amount of current exploratory research aimed at synthetic fuel refining, the availability of first generation technology, together with the long-term requirements for extensive synthetic fuel refining facilities, has delayed industrial commitment to a major effort in this field. Duplicating or supplanting these existing industrial research and development capabilities is undesirable. However, DOE support of basic and exploratory research leading to better understanding and improvements in synthetic fuel refining processes could result in earlier development of second generation processes.

A list of research areas is given in Table 2.8-3.

Table 2.8-3. Recommended research areas on the down-stream refining of coal-derived liquids.

a. Basic and Exploratory Research

1. Determinations should be made of the molecular structure of O, N, and S compounds and of polynuclear aromatics in coal oils and these data should be compared with results for typical petroleum fractions.
2. Mechanism for the removal of heteroatoms from coal oils by conventional catalytic hydroprocessing should be studied.
3. Alternate ways to remove heteroatoms from coal oils should be sought.
4. More active and more selective hydroprocessing catalysts are needed for heteroatom removal. The mechanisms and rates of these processes should be investigated.
5. The mechanism of those retrograde reactions should be studied that cause viscosity and solubility changes in some coal oils during storage.

b. Applied Research

1. The kinetics, selectivity, and catalyst deactivation steps in the hydroprocessing of coal oils for heteroatom removal should be studied.
2. Studies should be performed of the hydroprocessing of coal oils alone and in mixtures with petroleum stocks. Synergisms or antagonisms should be identified.
3. Investigations are needed to define the compatibility of coal oils with petroleum fractions after varying degrees of hydroprocessing.
4. Investigations are required of the potential health hazards (potential mutagenicity and oncogenicity) of coal oils after varying degrees of hydroprocessing.
5. Means must be found to optimize selectivity and catalyst life in the hydroprocessing of coal oils. These investigations should include a search for and evaluation of improved hydroprocessing catalysts.

c. Process Development

1. Additional economic studies are needed on the downstream refining of coal oils, including coal-oil and petroleum mixtures.
2. A systems approach should be employed in assessing the costs of refining and using these fuels. When are basically distinct coal-oil refineries economically desirable?
3. A systems approach should be applied to determine when modified engines to handle coal-oil products should be developed for selected end uses.
4. The development of advanced coal-liquefaction technologies should be pursued with proper allowance for downstream refining objectives.

d. Pilot Plants

1. It may be desirable to acquire or lease facilities for the experimental refining of coal-derived oils to produce standard products for engine development and fleet testing.
2. These facilities should be used for scale-up demonstration of optimal refining schemes.
3. Pilot-plant scale demonstrations should be initiated for the manufacture of hydrogen from coal-liquefaction bottoms streams.

e. Combustion Emissions and Health Problems

1. Emission from combustion of coal-derived liquids in existing and developing equipment should be assessed and control approaches defined where needed. Attention should be paid not only to SO_x , NO_x , particulates and smoke, but research should also address problems created by the presence of polynuclear aromatics, heterocyclics, and trace metals.
2. Threshold limits for exposure to polynuclear aromatics, polycyclics and trace metals should be defined.
3. Medical hazards associated with lighter aromatics (benzene, toluene) should be reexamined in view of the high concentrations of these molecules in coal-derived liquid streams.

CHAPTER 3:

COAL PYROLYSIS

3.1 Introduction

Pyrolysis occurs in virtually all coal-conversion and utilization processes and is an established coal-liquefaction route. Oil produced by hydro-liquefaction requires three times as much hydrogen per barrel of product as oil produced by pyrolysis. Pyrolysis has greater thermal efficiency than hydroliquefaction because of lower hydrogenation requirements; about half of the coal is converted to char. Coal-fired boilers are an incremental source of liquid fuels if the coal is first pyrolyzed to recover the hydrogen-rich volatiles and the carbon-rich char is then used for power generation.

3.2 Comments on Coal-Pyrolysis Technologies

Pyrolysis involves a primary thermal decomposition step generating volatile species, which undergo secondary degradation reactions until quenched. The yields and compositions of the primary products are determined by coal type and heating schedule. Higher rank coals and fast heating favor high primary liquid yields. Prolonged pyrolysis reduces the liquid yields and increases char and gas yields through secondary cracking and polymerization reactions. Stabilization of liquid-range precursors may occur by internal hydrogen transfer and by direct hydrogenation, which require high hydrogen pressure, catalysis, or both. Temperature, residence time, pressure, reactive gaseous and solid species, and catalysts are important parameters. In low-temperature carbonization in the absence of air (final char temperatures of 850-1400°F), at atmospheric pressure and in dense beds (fixed-bed retorts, continuously-moving bed retorts, and fluidized beds), prolonged exposure of volatiles leads to secondary cracking reactions and high char yields.

Rapid pyrolysis has been used near atmospheric pressure in an entrained-flow reactor. The small coal particles are heated very quickly and a high primary liquid yield results. Rapid breakup of the coal structure and fast vaporization minimize coke formation. Short vapor residence times and rapid quenching retard secondary cracking and polymerization reactions and maximize the net liquid yield.

In hydropyrolysis, dry hydrogenation is performed at hydrogen pressures of 500-2000 psi. In a fluidized bed, this process is referred to as hydrocarbonization. Rapid hydropyrolysis in an entrained reactor at short residence times is a recent development. The objective is to improve the yield and quality of the raw liquids.

Selected pyrolysis technologies are listed in Table 3.2-1. The liquid yields obtained by rapid pyrolysis and hydrolysis are seen to be nearly twice those achieved by carbonization with slow heating. The liquid yields from bituminous coal are generally 50% higher than from subbituminous coal. The maximum liquid yield is about 38%. The char yield is typically greater than 50%. Rapid pyrolysis and hydrolysis liquid yields are roughly equivalent.

The direct products of pyrolysis generally require further processing. The liquids require hydrogenation to reduce the molecular weight and remove heteroatoms. However, sufficient H_2 for these purposes is generally available from reforming of the pyrolysis gases. The sulfur content of the raw char is about the same as of the parent coal. Utilization of the char as fuel therefore requires desulfurization and gasification, followed by clean-up or post-combustion control. Although hydrolysis liquids are preferred over the products derived from rapid low-pressure pyrolysis, the maximum yield is about the same and hydrofining is still required.

A. The Lurgi Ruhrgas Process

This low-pressure pyrolysis process was developed for the liquefaction of European brown coals and is the only pyrolysis process presently in commercial use. A 1,600 tpd Lurgi-Ruhrgas plant was built in Yugoslavia for lignite and operated successfully. The char is fired in an adjacent power plant. Coal is crushed to one-quarter inch size and is then fed into a mechanical mixer, where it is rapidly heated to 850 to 1100°F by direct contact with hot, recirculated char that was previously heated by partial oxidation with air in an entrained-flow heater. Net product char is withdrawn. The gases from the mixer are passed through a cyclone for particulate removal and then through condensers to collect liquid that is further hydro-treated to form a range of products.

B. The COED Process

The COED (Char-Oil-Energy-Development) process of the FMC Corporation has been under development since 1962 and produces a synthetic crude oil by fluidized bed pyrolysis and separate oil hydrotreating. Following testing in a 100 lb/hr PDU, a 36 tpd pilot plant was built (1970). Tests with durations in excess of 30 days were completed before the plant was dismantled. Another pilot plant to evaluate gasification (COGAS) began operation in 1974. A conceptual commercial COED design (Ralph M. Parsons Co., 1975) produces 28,000 bpsd of 25° API syncrude from 27,400 tpsd (21,500 tpsd, MAF basis) HVCB bituminous coal. Minus 6 mesh crushed coal is processed at atmospheric pressure in fluidized beds in which agglomeration is prevented by operating at successively higher temperatures. Three pyrolysis stages

Table 3.2-1 Summary of pyrolysis technologies; liquid yields refer to maximum reported amounts.

Process/ Developer	Reactor Type	Residence Time of		Temper- ature °F	Pres- sure, psia	Coal type	Liquid yield in wt. % (MAF)	Status and comments
		coal	gas					
Fixed-bed retorts	fixed-bed	> 4 hr.		850-1400	~15		6-12	Obsolete; extensive commerical opera- tions in Europe.
Lurgi-Ruhrgas	mechanical mixer/con- veyor	> 20 sec.		1110	~15	Brown	24	A 1600 TPD plant has operated in Yugoslavia since 1963.
COED, FMC	multiply- staged, fluidized beds	1-4hr.		575, 815, 1050, 1600	~25	HVCB Sub. C	22 12	A 100 lb./hr. PDU operated 1976-70; a 36 TPD pilot plant operated 1970-75.
Flash pyrolysis, Occidental	entrained flow	1-3sec.	1-3sec.	1200	~60	HVCB Sub. C	35 22	A 3 TPD PDU oper- ated 1976-78.
Hydrocarboniza- tion, Union Car- bide	fluidized bed	5-12min.		1050 1040	940 310	Sub. C Sub. C	29 21	1, 10, and 1500 lb./ hr. units operated in the 1960s.
Flash hydro- pyrolysis, Rockwell	entrained flow	>100msec.	>100msec.	1570-1770	500- 1500	HVCB	38	A 1 TPH reactor operated 1976-78.
BNL	entrained flow	1-10sec.		1380	2000	Lignite	20	A 10 lb./hr. bench scale unit has opera- ted since 1975.

operate at 575, 815, and 1050°F, respectively; generally, the temperatures and the number of stages depend on the agglomerating properties of the coal. Representative performance data are listed in Table 3.2-2.

Hydrotreating of the raw oil in an ebullating bed reactor yields 25% product oil of -250°F, 40° API, 0.07% naphtha and 75% of +250°F, 4.6° API, 0.5% fuel oil. Hydrogen consumption is 1700 SCF/bbl. The high boiling fraction of the oil product from the hydrotreater contains char fines entrained from the pyrolysis section and is recycled to the pyrolysis reactors, where the oil is converted to char and lighter oil products. Agglomeration problems were experienced with both Kentucky and Illinois coals, which have free swelling indices of about 4-5. The char yield from bituminous coal was about 60%, with a sulfur content approximately equal to that of the parent coal. Several char-utilization schemes have been investigated at FMC, including gasification, desulfurization, and direct combustion in a utility boiler. Partial gasification was successfully demonstrated in the fourth-stage reactor of the pilot plant.

C. Rapid Pyrolysis

Studies on rapid pyrolysis have been performed, especially at the Rockwell Corporation and at the Occidental Petroleum Corporation. These studies are discussed in connection with the site-visit reports summarized in Sections AC-9.1 and AC-9.2.

D. Hydropyrolysis

In hydropyrolysis, coal is pyrolyzed under elevated hydrogen pressure to effect direct, dry, gas-phase hydrogenation of the primary volatiles as they are evolved in the pyrolysis reactor. Since the primary volatiles are unstable and tend to undergo secondary cracking and free radical condensations, the presence of molecular hydrogen can alter the reaction paths and lead to improved liquid yield and quality.

Hydrocarbonization is a fluidized bed process that is conducted under relatively moderate conditions (300-1000 psi hydrogen pressure, temperatures of 950-1100°F, and coal and vapor residence times up to 25 seconds). The liquid yield generally increases with hydrogen pressure. In flash hydropyrolysis (FHP) using entrained-flow, hydrogenation occurs at short residence times. The influence of severe conditions is being investigated (temperatures to 2000°F, pressures of 4000 psi, and contact times as low as 0.03 second). One objective of this approach is to achieve high primary oil yields with rapid pyrolysis while effecting gas-phase hydrogenation at short contact times. For details, reference should be made to the site visit reports in Section AC-9.1.

Table 3.2-2 COED liquid yield and characterization data.

<u>Coal</u>			
Rank	Bituminous C	Bituminous C	Subbituminous C
Source	Illinois No. 6	W. Ky. Nos. 9 & 14	Big Horn, Wy.
<u>Yield</u> (MAF basis)			
Wt. %	21.7	19.6	12.2
Bbl/ton	1.1	1.0	0.63
<u>Analysis</u>			
Ultimate, Wt. %			
C	81.5	81.9	82.7
H	7.8	7.5	8.0
N	1.0	1.2	1.0
S	2.4	1.6	0.6
O	7.1	7.7	7.5
Atomic H/C	1.15	1.10	1.15
Gravity, °API	-4.0	-4.8	-4.0

E. The Hyderabad Process

At India's Regional Research Laboratory (RRL), Hyderabad, an improved version has been developed of the Lurgi Spuelgas Process for the low-temperature carbonization of coal. The program involves carbonizing 20 to 100 mm lumps of subbituminous coals from Indian mines; the semi-coke product is a substitute fuel for wood charcoal. The Lurgi Spuelgas Process employed brown coals and lignites. In the Hyderabad process, better feedstock (subbituminous coal) is used with improved thermal efficiency. A pilot plant carbonizing 25 tpd was operated for a number of years. A commercial plant for 1,000 tpd has been operational since late 1978. In mid-1979, capacity expansion to 3,000 tpd (2050 tpd of semi-coke product) was authorized; tar output will be about 180 tpd and the plant will also produce about 500,000 Nm³ per day of low-Btu gas.

3.3 Summary of Research Needs in Pyrolysis

We list here identified research needs relating to the development of improved methods of coal pyrolysis.

- (i) A comprehensive model of pyrolysis is needed to relate yields and product distributions to coal type and process conditions. This model will require elucidation of the controlling chemistry and transport phenomena and should permit optimization of yields and product distributions, as well as process scale-up.
- (ii) Reliable thermochemical data are needed for the polynuclear aromatics, radicals, and coal fragments which may exist as intermediates in coal pyrolysis.
- (iii) Additional information is required on the primary coal-decomposition reactions (e.g., the mechanisms, rates, and primary products as functions of coal type and reaction conditions).
- (iv) Further work is needed on the fluid mechanics and dynamics of molten particles. The mechanisms of bubble formation, movement of volatile species out of the decomposing particles, and pressure developments within coal particles should be studied, with emphasis on the porosity and reactivity of the residual char.

- (v) Control of free radicals during pyrolysis is required to optimize liquid yields. Recombination of free radicals, formed in the primary pyrolysis, with the parent coal or with other large free radicals, will lead to the loss of liquids. Control of coal-surface reactivity and the introductions of chain-transfer catalysts (e.g., HCl or H₂S) and gas-phase Lewis acids (e.g., BF₃) should be investigated.
- (vi) The use of oxygen during pyrolysis to stimulate oxidative degradation has been suggested and may be worth examining.
- (vii) The impacts of disposable catalysts and of native mineral matter must be better understood. The effects of clays, alkalis and pyrites on liquid yields should be studied.
- (viii) The impact of yield on product quality should be defined. Does higher liquid yield necessarily produce liquids of lower quality (i. e., liquids more deficient in hydrogen) and stability? The selectivity for hydrodesulfurization and hydrodenitrogenation under hydropyrolysis conditions should be determined.
- (x) The reactivity of char formed from caking and non-caking coals should be investigated. We need to know how these chars behave as boiler fuels.
- (xi) Uninterrupted, long-term support is required if rapid coal pyrolysis is to be developed successfully for commercial applications.
- (xii) Supporting research is needed to assure better instrumentation and diagnostic measurements than are currently made. Model flow studies may be useful, especially for successful scaling.
- (xiii) It would be desirable to compare pyrolysis yields for oxygen-free coals with those obtained under presently used conditions of feed preparation and injection.

CHAPTER 4:

COSTING OF COAL LIQUIDS

Presentations were made on coal liquefaction economics by representatives of four of the active groups working on coal liquefaction (see Appendix AC-10 for details). The purpose of the discussions was not a comparison of relative process economics but rather the identification of specific process areas where improvements might lead to significant economic benefits.

Economic data presented on the four processes referred to different bases (i. e., form of financing, project life, tax credits, etc.). In Table 4-1, all costs were adjusted to 1979 dollars at 7%/yr. and then distributed to major process cost areas. No attempt was made to place all of the processes on the same economic basis. Costs of coal liquids will vary widely because of the economic bases chosen. In addition, the levels of investment will also vary, based on the amount of engineering detail involved and the project/process contingencies included. The plant capacity factor that is used also plays a significant role in determining product cost. Reference to Table 4-1 shows that the capital costs, either on a per ton or per barrel of liquid product basis, are high. As the result, the capital charges are the major component in the final product costs, independent of the form of financing and investment credits used. The distribution of capital costs shows that the cost of hydrogen manufacture approaches that of the basic liquefaction process facilities.

We now proceed to identify those areas where additional research and development may lead to improved technologies and better economics, especially reductions of capital costs. In general, little can be done about the coal feed cost itself. Improvements in that area require increased mining or transportation efficiencies. We note especially the following desirable goals: process simplification, new catalysts that have improved selectivity for producing liquid products and thus lower hydrogen consumption, and process improvements of all types, for example, the development of processes for operations at lower pressures. The high relative cost of hydrogen manufacture has led to the generally accepted view that improvements in gasification processes are as important to the nation in achieving direct coal liquefaction at acceptable costs as they are for SNG production, power generation, and indirect coal liquefaction. An important area for improvement in the overall economics for direct coal liquefaction relates to improvements in the quality, as well as in the quantity, of the liquid product output. The costs of refining coal-derived synthetic crudes to marketable products are not insignificant. Hence, better processes and catalysts for the primary coal-liquefaction step will reduce downstream refining costs and thereby reduce the overall costs for producing specification products for the market. Higher coal conversions and reduced gas-make will also increase the total

number of barrels of distillate products for a given plant investment, thus reducing the costs per barrel. However, an important consideration to bear in mind is the "balanced plant" concept of a coal liquefaction facility. All streams must have an ultimate disposition and there is a need to assure that all hydrogen and fuel requirements can be met. For example, increased conversion would reduce the amount of bottoms produced. If there are insufficient bottoms to produce the needed hydrogen, additional hydrogen must be brought into the system, usually by bringing in some coal directly for hydrogen production.

Table 4-1. Costs and cost distributions in coal liquefaction.

	Range for EDS, SRC-II, Dow and Zinc Chloride Processes
Capital cost, \$/T/CD	54,900 - 96,300
Liquid products, Bbl/T	1.9 - 3.5
Capital cost, \$/Bbl	15,700 - 47,000
<u>Capital cost distribution, %</u>	
Liquefaction	18.0 - 35.7
Hydrogen manufacture and cleanup	15.2 - 41.2
Other (power, utilities, tankage, offsites)	40.1 - 63.5
<u>Total costs, % (feed, capital charges, operation)</u>	
Coal	11 - 35
Capital charges	38 - 62
Operating costs	26 - 27

Note: All costs are adjusted to 1979 dollars at 7%/yr. No attempt was made to place all of the processes on the same economic basis, except that 1979 dollars are used.

APPENDIX A:

FERWG-II STATEMENT OF WORK

The objective of this project is to conduct an independent assessment providing for identification of the long-range research needs associated with coal liquefaction. This work is expected to include recommendations to DOE for research programs that can best contribute to the successful long-term development of new coal-liquefaction technologies.

The contractor shall provide the necessary personnel, facilities, services, materials and documentation required to perform all of the required tasks.

In fulfillment of the project objectives, the contractor will be expected to work with both the academic community and industry. The assessment will consider all of the basic disciplines involved in the development of coal-liquefaction technologies. The researchers will be expected to gain first-hand familiarity with operational aspects of the gasification technologies through site visits, interviews, examination of development studies and reports, and other means.

Typical of the kinds of long-range issues that will be addressed are the following:

1. How much cheaper or more efficient may we expect coal-liquefaction technologies to be in the future compared with those that are now in use or under development?
2. Can we identify the scientific and engineering directions that will be useful in making these technological improvements?
3. What scientific and technical areas that are key to the success of ongoing coal-liquefaction R&D are still "open" areas for research, i. e. areas likely to profit from a broader or deeper look?
4. What disciplinary or interdisciplinary fields or research ideas should be supported because they hold long-range potential for generating innovative and useful technologies?

In complying with the objectives, the contractor shall perform the following tasks.

Task 1: Prepare a Detailed Work Plan

The contractor will prepare a work plan for DOE review and approval that will define the execution of the remaining two (2) tasks. This detailed work plan will include documentation of the following activities:

Description of a methodology for obtaining independent assessments representing a wide diversity of views concerning coal-liquefaction technologies.

Site-visits as required.

Technical approach for evaluating research needs for each project. The work plan will be submitted for approval by the DOE technical representative. DOE comments shall be furnished to the contractor within 5 working days after receipt.

Task 2: Conduct Assessment

In accordance with the detailed work plan (Task 1), the contractor shall conduct the necessary research and assessment activity. It is expected that a credible assessment will require use of a variety of information sources, including:

Site-visits to liquefaction-related projects to gain first-hand familiarity with currently available or developing liquefaction, technologies, including operational aspects; technical discussions with government, industrial, and research community specialists in coal liquefaction; review of relevant technical literature; other means as deemed appropriate, including the use of consultants from industry and the academic research communities.

The contractor will submit to DOE an interim letter report describing each site visit and significant technical meeting during this assessment.

Task 3: Prepare Final Report

The contractor will prepare a final report of this assessment for DOE. This report will include the following:

Purpose of study; study approach; list of consultants, if any, and other information sources; brief description of sites/projects visited; research needs identified, according to technology area, urgency, and expected benefit time-frame; recommendations.

SCHEDULE

- Item 1: The Detailed Work Plan in accordance with Task 1: June 1979.
- Item 2: A draft report on each site visit in accordance with Task 2:
three (3) weeks after each site visit.
- Item 3: Final Report, including Identification of Research Needs for
Coal-Liquefaction Technologies in accordance with Task 3:
March 1980.

APPENDIX B:
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APPENDIX C

SELECTED REPORTS OF SITE VISITS,
CONFERENCES AND DISCUSSIONS

This section contains edited copies of site-visit and other reports prepared by FERWG members. Some of the hand-out materials prepared by DOE contractors and others are included (without explication) to permit readers the construction of a coherent picture of work in progress.

AC-1.1 REPORT OF SITE VISIT TO THE
SRC FACILITIES AT FT. LEWIS, WASHINGTON
(MAY 11, 1979; VISITORS: F. LEDER, S. S. PENNER,
E. REICHL, J. ROSS, R. SIEG, A. SQUIRES, L. TOPPER)

A. Research Needs

Discussions were held with John Ward (plant manager) and other SRC staff members, including J. Naylor, D. Canfield, and J. A. Segerson. R. Hamilton (Section Chief, Coal Liquefaction, DOE in Washington) also participated. The current status of the SRC-I and SRC-II programs was reviewed, including the authorized scale-up to a 6000 ton per day SRC-II demonstration plant.

Only about one half of the active volume of the dissolver is used in SRC-I. The residence time of the reactants in the dissolver is about 1 hour in SRC-II. The detailed flow behavior in this critical unit is not now well understood. For this reason, radioactive tracer studies of "backmixing" have been proposed in support of numerical model development for scaling by Norman Carr (Gulf R and D, Harmorville, Pa.). These studies are now in progress.

A visit to the facilities and dialogue with plant personnel (Duane Konen, David Williams, Fred Von Bargaen) provided informative insight into plant operational problems.

Although SRC-II has operated successfully for 160 days, FERWG members attempted to identify hardware and operational problems which might profit from R and D activities that are performed concurrently with the scale-up of the SRC-II reactor to the demonstration plant at Morgantown, W. Va. The following listing is indicative of the topics that received attention in this connection:

1. Continued development activities are needed for let-down valves, especially for the handling of coal slurries. Let-down valves now last about six to twelve weeks. However, scale-up may lessen the trim breakage problem and lead to longer useful life.

2. The development of rheological models for coal slurries should be supported.
3. The design of a practical and inexpensive method for the preparation and blending of the coal feed should be supported in order to maintain uniform coal-feed properties. A computer-controlled procedure, of the type that has been used in Japan for the preparation of coke-oven feed, was suggested.
4. Methods for the identification and elimination of plugging need to be developed. Plugging has been the principal cause of shut downs: it has been associated with start-ups, shut-down or operator error and may be the result of local failures of electrical heating (plugging by chilling) or by repolymerization in the absence of adequate amounts of hydrogen (especially at elevated temperatures). Critical concentration ranges for operation without plugging must be defined.
5. The development of an on-line viscometer for measurements on slurry-filled pipes would provide a useful operational tool.
6. Reliable pumps must be identified or developed for handling vacuum-tower bottoms.
7. Corrosion problems can probably be handled by selecting the right type of steel. The relation of corrosion rate to chloride concentrations should be studied. Corrosion rates have been high in the middle fraction distillation column. There is a substantial temperature difference between two adjacent distillation columns. Observed chloride concentrations range from 6 to 200 ppm and chlorides in the oil may be corrosive.
8. A better solution than hastalloy needs to be found for the control of chloride corrosion.

9. Coking occurs on the pipes over long periods of time. The coke falls off periodically (during temperature cycling, start-up or shut-down). A device for measuring the rate of coke build-up on interior pipe walls and better knowledge of the mechanism of coking in the dissolver environment would be useful.
10. The nature of regressive reactions should be studied. We require definitions of allowable windows for hydrogen, hydrocarbons, stable coke build-up, etc. The early mesophase material is probably very sticky but formation may perhaps be reversed through introduction of appropriate hydrogen concentrations. Perhaps a "dirty" reactor can be run that will effectively isolate small (i.e., micron-size) mesophase material as it is formed and prevent its agglomeration to large domains.
11. Microscopic examinations of early residue formations may be useful.
12. A "run-away" reaction in the dissolver is probably not possible. Temperature spikes to $\sim 930^{\circ}\text{F}$ have been produced when the pre-heater outlet temperature was not used adequately for control of the reactor temperature; the normal reactor temperature is $\sim 850^{\circ}\text{F}$. It might be useful to attempt identification of operational conditions needed for run-away reactions to occur.
13. The development of reliable control units, tied to a few important measurements, should be supported.
14. The relation between variability in coal-feed input and unit output requires study. Much useful information has been assembled empirically and will presumably be obtained also during operation of the demonstration plant.
15. Scale-up of preheater designs to commercial scale is uncertain and requires study.

B. Process Data

A schematic diagram of the Fort Lewis SRC-II facility is shown in Fig. AC-1.1-1. Eighty percent of the coal is fed in at a size range that will pass a 200-mesh screen. The total slurry feed rate is about 6000 lbs/hr of which about 2000 lbs/hr are coal. After drying, the moisture content is less than $\frac{1}{2}\%$. The slurry blend tank is maintained near 350°F. The dissolver is at about 2000 psi and the slurry preheater at a somewhat higher pressure while a temperature of 750-800°F is reached. The inlet H₂-gas velocity (which may enter from one or more of three possible injection-port locations near the top, middle, and bottom of the dissolver) is fairly high. The normal entrance temperature to the dissolver is 750-800°F while the exit temperature is 860°F. The residence time in the dissolver is about 1 hour at a pressure of 2000 psi. The letdown system takes the material in two stages to about 150 psi.

Figure AC-1.1-2 shows a chronological summary of pilot-plant experience at Fort Lewis. Material balance and yield data for SRC-II are shown in Table AC-1.1-1 for controlled, equivalent feed material. The data show that the total output of distillates varies by about 15%. SRC-II product yields are shown in Table AC-1.1-2. The data summarized in Table AC-1.1-3 refer to results obtained with coals from three different mines. The SRC yields are seen to vary by more than 50% while the total distillate yields vary by about 40%. Comparison of the results shown in Tables AC-1.1-1 and AC-1.1-2 indicates that changes in coal feed produce substantially larger output variations than correspond to normal process variability. Results obtained in a materials balance test are given in Table AC-1.1-3.

C. Comments on Increasing the Probability of Successful Scale-Up of SRC-II

The following comments are offered in the hope that they will increase the chances of success in extrapolating the current 24 ton/day pilot plant results to a 3000 ton/day reactor system. This 125:1 scale-up ratio is proposed for the 6000 ton/day, 2 train, SRC-II demonstration plant at Morgantown, West Virginia.

Fig. AC-1.1-1 Schematic diagram of the Fort Lewis SRC-II pilot plant.

Fig. AC-1.1-2 Chronology of operating experience at the Fort Lewis SRC pilot plant.

Table AC-1.1-1 Material balance and yield data for the SRC-II pilot plant.

MATERIAL BALANCE RESULTS - ELEMENTALLY BALANCED YIELDS - DISTILLATE YIELDS BASED ON PCM DISTILLATION PROCEDURE

Conditions	Run 78SR-22	Run 78SR-23	Run 78SR-24	Run 78SR-25	Run 78SR-26	Run 78SR-27	Run 78SR-28	Run 78SR-29	Run 79SR-30
Dehumidified Coal Feed, lb/hr	2108	2072	2089	2104	2038	2089	2072	2136	2099
Feed Slurry Composition, wt%									
Coal	29.2	27.1	27.9	30.9	30.3	30.2	30.6	31.3	27.6
Mid. Dist (350°-450°F)	1.9	3.2	8.3	6.7	6.6	1.5	1.6	2.3	2.3
Hvy. Dist (450°-850°F)	28.2	26.9	21.8	21.1	25.2	27.6	29.5	25.5	27.3
SRC	25.5	26.6	25.1	24.7	23.3	27.0	25.1	27.0	26.4
Ash (due to recycle slurry)	10.2	11.0	11.3	10.7	9.6	9.1	9.2	9.4	9.6
ICM (due to recycle slurry)	5.0	5.2	5.6	5.9	5.0	4.6	4.0	4.5	4.2
Iron (total in feed slurry)	1.97	2.25	2.25	2.25	2.05	1.99	2.22	2.36	
Hour Space Rates, lb/hr ft ³									
Coal	22.9	22.5	22.6	22.9	22.7	22.7	22.5	23.2	22.8
Total Slurry	78.5	83.2	81.4	73.6	74.8	75.1	73.6	74.1	76.8
Nominal Dissolver Res. Time, hrs	0.91	0.86	0.88	0.97	0.96	0.95	0.97	0.97	0.93
Hydrogen Purity, Mole %	85.6	85.6	86.0	84.7	85.7	85.9	85.5	86.0	83.2
H ₂ /Slurry Ratio, lb H ₂ /100 lb slurry	4.35	4.66	4.96	5.06	5.35	5.56	7.13	6.70	5.18
Dissolver Pressure, psig	2005	2007	2003	2005	2004	2003	2003	2008	2002
Average Dissolver Temp., °F	853	852	853	860	857	852	852	851	851
Feed Coal	Powhatan #5	Powhatan #5	Powhatan #5	Powhatan #5	Powhatan #5	Powhatan #5	Powhatan #5	-1/3" Powhatan #5	30 and 40 #5
Ash in Moisture Free Feed Coal	11.24	11.76	11.47	11.24	11.79	10.53	9.99	12.32	11.51

ELEMENTALLY BALANCED YIELDS, based COAL FEED

Component	Run 78SR-22	Run 78SR-23	Run 78SR-24	Run 78SR-25	Run 78SR-26	Run 78SR-27	Run 78SR-28	Run 78SR-29	Run 79SR-30
H ₂	-4.5	-4.6	-5.5	-5.2	-4.7	-3.9	-4.5	-4.5	-4.4
C ₁	5.5	7.4	8.8	8.5	6.8	6.0	6.6	6.3	6.8
C ₂	4.0	4.3	5.2	5.1	4.1	3.8	4.2	4.1	4.0
C ₃	3.2	3.7	4.6	4.8	3.7	3.6	4.1	4.0	4.0
C ₄	2.2	2.1	2.9	3.3	2.4	2.2	2.7	2.5	2.5
CO	-1.7	-0.1	0.2	-0.7	-0.5	-0.6	0.0	-0.6	-0.6
CO ₂	2.0	1.9	1.4	2.3	1.3	1.6	1.3	1.5	1.2
H ₂ S	2.3	2.3	2.6	2.6	2.5	2.7	2.7	2.4	2.6
NH ₃	0.5	0.5	0.6	0.5	0.5	0.4	0.6	0.6	0.6
Water	6.3	7.4	6.8	6.8	7.5	5.0	5.8	6.4	5.7
ICM	6.2	6.4	6.1	7.1	6.3	5.7	4.8	5.0	6.0
Naphtha + C ₅ ⁺	10.4	7.6	11.5	9.7	12.8	9.0	5.6	7.7	7.1
Mid. Dist.	30.7	21.6	22.7	21.7	28.4	28.1	22.3	19.3	23.3
Hvy Dist.	2.2	12.4	6.5	5.8	0.8	6.0	17.6	17.1	9.6
SRC	30.7	27.7	25.6	27.7	28.1	30.4	26.2	28.2	31.6
Fusion Point, °F	363	354	333	349	351	364	315	333	312
% Solids in Vcc. Btms.	38.0	41.6	42.8	41.6	41.1	36.5	37.9	40.3	38.2

Table AC-1.1-2 SRC-II product yields.

<u>Coal</u>	<u>K. Ky.</u>	<u>Ill. #6</u>	<u>Pitt. Seam</u>
Dehumidified Coal Feed Rate, lb/hr	1984	2008	1998
Kg/hr	900	911	906
Feed Slurry Composition, wt %			
Deh. Coal	29.5	29.5	30.3
Solvent	33.4	35.6	29.8
SRC	23.9	20.0	24.1
Ash (due to recycle slurry)	8.2	11.0	8.3
IOM (due to recycle slurry)	5.0	3.9	7.5
Nominal Dissolver Residence Time, hrs	0.98	0.97	1.00
Hydrogen Purity in Feed Gas, mole %	89.8	93.7	91.6
Average Dissolver Temperature, °C	461	457	456
°F	861	854	855
Dissolver Pressure, MPa	13.34	13.44	14.09
psig	1920	1934	2029
<u>Yields, wt % M.A.F. Coal</u>			
Hydrogen Consumption	-4.8	-4.7	-3.5
Hydrocarbon Gas (C ₁ to C ₄)	18.4	15.8	15.5
Naphtha	14.2	17.0	11.9
Middle Distillate + Heavy Distillate*	28.2	30.3	22.3
SRC*	26.1	23.0	36.8
IOM (unreacted coal)	6.6	5.0	11.9
Total Distillate Yield** (bbl/ton M.F. coal)	2.27	2.46	1.89

*Adjusted to produce a vacuum bottoms product with a 177°C (350°F) fusion point.

**Naphtha, Middle Distillate, and Heavy Distillate

Table AC-1.1-3 Results obtained in a material balance test.

Operating Conditions

Coal	Western Kentucky #9/#14	
Moisture Free (M.F.) Coal Feed Rate	1837.0 Kg/hr	(4050 lbs/hr)
Solvent Feed Rate	2860.4 Kg/hr	(6306 lbs/hr)
Hydrogen Purity in Feed Gas	94.1 mol %	
Hydrogen Feed Ratio	529 cu m/	M.T. moisture free coal feed
Dissolver Outlet Temperature	451°C	(846°F)
Dissolver Pressure	10.33 MPa	(1484 psig)

Product Yield

% M.F. Coal

Hydrogen	-2.4
Methane	1.4
Ethane	1.0
Propane	0.9
Butane	0.4
Carbon Monoxide	0.0
Carbon Dioxide	0.8
Hydrogen Sulfide	1.4
Water	5.0
Light Oil	5.1
(Ambient - 193°C)	
Wash Solvent	4.0
(193°C-249°C)	
Process Solvent	4.4
(249°C-454°C)	
SRC	63.0
Ash	9.6
Unreacted Coal (IOM)	5.3

No advice is offered with regard to the following critical questions:

- (a) Is the demonstration at a 6000 ton/day scale to be recommended?
- (b) Is the processing of the vacuum-tower bottoms ready for larger scale application by the Texaco process?

Comments on the SRC-II mode of operation:

(1) The slurry preheater is one of the critical items of equipment. The present 3" tube heater, or a new 2" tube heater, will be further studied to yield data for plant design. A detailed description of heater design should be included in Phase O - Scope of Work to assure that the extrapolation is as safe as possible.

(2a) Dissolver

The projected extrapolation in handling capacity is 125:1 for the unit at Ft. Lewis. However, extrapolation from German commercial units is 10 to 1 or less. Although German operating conditions were at 50 to 100% higher pressures, the basic operations of the slurry phase reactor (using gas circulation as a source of agitation) are quite similar. An attempt should be made to find German engineering data for sump-phase hydrogenation reactors in the current review of German documents conducted at Texas A&M; DOE should arrange access to this project for the SRC-II managers.

(2b) Dissolver Model

It is recommended to include (in the scope of Phase I of the demonstration-plant project) a cold model for the proposed full-size reactor to study the 3-phase system for channeling and settling techniques. A program using radioactive tracer particles is now scheduled at the Tacoma plant.

This study will be useful to assure better understanding of the behavior of solid, liquid and gas flows under process conditions.

(3a) Vacuum Tower

The low-pressure, hydrogen-free section of the process is apparently the more difficult part of the system to use, from the point of view of operating reliability. This difficulty results from the high tendency for coking of the heavy primary product. The SRC conditions are much milder than those used in German commercial experience and the resulting product is far less stable.

To obtain better operating reliability, improved knowledge must be gained of the condition of the vacuum-tower inventory. Measurements of viscosity and/or solids concentration would be helpful. It is suggested that on-line instrumentation be explored for this purpose (e.g., a Stormer viscometer).

(3b) Vacuum-Tower-Bottoms Pump

Development of a reliable positive displacement pump for handling the vacuum-tower-bottoms stream should prove helpful. We learned that this work is already in progress. Availability of such a pump may obviate the need for the costly high elevation of the vacuum flash unit that is now used.

(4) Slurry Handling

It is evident that a great deal of very valuable detailed mechanical and operational know-how has been accumulated at Tacoma. Much of this now resides in the experienced operating crews, at all levels.

It is particularly important for the scale-up project that this know-how is applied, to the maximum extent possible, in the detailed mechanical

design of the demonstration plant. The plant operators should be given specific time to review the mechanical layouts in great detail (particularly piping details) and the plan of work should include specific time and money for changes requested by this review. There is no way to replace this operational know-how by "science".

(5) Philosophy in Designing the Demonstration Plant

The SRC processes (I and II) operate under conditions of low severity, at least insofar as complete degradation and conversion of coal to liquid are concerned. As a result, the processes are not very "forgiving" to errors, particularly in the downstream sections (deashing, vacuum distillation).

It would be best to design the demonstration plant with some leeway as far as the severity of processing conditions is concerned. Thus, plant reliability may require some increase in both maximum H_2 pressure and maximum H_2 circulation rate. It is recommended that this extra capacity (above the base-case) be provided in the demonstration plant, in spite of the obviously higher cost.

AC-1.2 REPORT OF SITE VISIT (OCTOBER 22, 1979)

TO THE GULF OIL RESEARCH LABORATORY,

HARMARVILLE, PA.

The primary purposes of the site visit to the Gulf Oil Research Laboratory at Harmarville, Pa., were further discussions of the SRC-II experience and program plans, with special reference to completed studies on the P-99 PDU, modeling and scaling. The following FERWG members participated: Clardy, Furlong, Leder, Penner, Ross, Sieg, and Squires. The group was joined by I. Wender (Fossil Energy) and R. H. Kropschot (Office of Basic Energy Sciences) of DOE and by R. F. Bauman of the Exxon Baytown Research Laboratory. Discussions were held with the following staff members of the Gulf Oil Research Laboratory: N.L. Carr (Gulf Research and Development Center, GR&DC, C&MD), H. G. McIlvried (GR&DC - C & MD), K. Parimi (GR&DC - C&MD), J. L. Stephenson (GR&DC), R. G. Sperhac (GMRC), and others.

The following formal presentations were made:

McIlvried, P-99 Operations;

Carr, Mathematical Modeling and Correlation Work;

Stephenson, Physical Properties;

Parimi, Correlation and Equipment Design.

A. The SRC-I Process

A flow diagram showing the SRC-I process is reproduced in Fig. AC-1.2-1.

Fig. AC-1.2-1 Schematic diagram showing the SRC-I process.

B. P-99 PDU Studies on the SRC-II Process

A schematic diagram of the SRC-II process is shown in Fig. AC-1.2-2. A simplified flow diagram for the P-99 PDU is reproduced in Fig. AC-1.2-3. The P-99 PDU is designed to utilize 1 ton of coal per day but has usually been operated at a one half ton per day utilization rate. Program objectives are summarized in Table AC-1.2-1. Operating schedules are indicated in Fig. AC-1.2-4. The coals that have been tested in the P-99 PDU are listed in Table AC-1.2-2 while Table AC-1.2-3 shows the ranges of operating conditions used (these include anticipated process conditions for each of the listed variables in the demonstration plant). The P-99 feed and product streams and the corresponding methods of measurements are summarized in Table AC-1.2-4.

A listing of needed or measured physical and thermal properties data appears in Table AC-1.2-5.

We refer to our earlier site visit report (dated May 11, 1979) for detailed comments by FERWG members on the Ft. Lewis SRC-II studies and for recommendations concerning the large demonstration plant which is currently under construction. Here we confine further detailed assessments and recommendations to remarks on modeling and scaling.

C. Modeling the SRC-II Dissolver; Management Problems

Workers at Gulf claim to have a good model for the hydrodynamics and chemistry of the SRC-II dissolver. However, only broad general statements about the model were made to FERWG. Modeling was funded by Gulf until January 1, 1979; the contract for DOE support of the effort from this date onward is not yet complete; until Gulf has been paid retroactively for work performed this year under the new contract, details of the model will apparently not be divulged.

Fig. AC-1.2-2 Schematic diagram showing the SRC-II process.

Fig. AC-1.2-3 Simplified flow diagram of the P-99 facility.

Table AC-1.2-1 Program objectives of the SRC-II pilot-plant studies.

DEMONSTRATE PROCESS OPERABILITY

Accomplished; stability has been verified.

Use bituminous coals: Kentucky, Illinois and Pittsburgh

Seam coals have been run; the ash is satisfactory.

Beneficiated coal has been tried.

OBTAIN YIELDS AS A FUNCTION OF OPERATING CONDITIONS
AND COAL SOURCE

TEST EQUIPMENT CONFIGURATIONS

PROVIDE DESIGN DATA

Fig. AC-1.2-4 Operating schedules followed for Kentucky coal; the lengths of the lines measure the test durations.

* Christmas

† Summer

AC-19

Table AC-1.2-2 Coals run in the P-99 program.

A steady-state point is defined in 5-7 days; a materials balance is done once per day. All coals are deep-mined. There is very little difference in process solvents for different coals.

KENTUCKY COAL	11 RUNS
---------------	---------

PITTSBURGH SEAM COALS

BLACKSVILLE	6 RUNS
-------------	--------

IRELAND	2 RUNS
---------	--------

POWHATAN (I)	3 RUNS
--------------	--------

VALLEY CAMP	2 RUNS
-------------	--------

ROBINSON RUN	4 RUNS
--------------	--------

POWHATAN (II)	3 RUNS
---------------	--------

POWHATAN (III)	8 RUNS
----------------	--------

POWHATAN (IV)	2 RUNS
---------------	--------

Table AC-1,2-3 Range of operating conditions used in the P-99 program.

PRESSURE	2000 - 2500 PSIG
TEMPERATURE	851 - 869°F
SLURRY RESIDENCE TIME	0.7 - 1.3 HR.
COAL CONCENTRATION	25 - 40 WT %
GAS CIRCULATION RATE	48000 - 89000 SCF/T
GAS PURITY	80 - 94 VOL % H ₂
TOTAL FEED SOLIDS	40 - 49 WT %

Table AC-1.2-4 P-99 feed and product streams.

<u>Feed</u>	<u>How Measured</u>
Coal	Weigh Belt
Make-up Hydrogen	McAfee Gauge
Flush Water	Calibrated Tank
Flush Oil	Calibrated Tanks Minus Weight of Flush Oil Leakage
 <u>Product</u>	
Excess Process Solvent	Change in Inventory of all Tanks
Debutanizer Bottoms	Weigh Cells
Vacuum Tower Bottoms	Scales
Process Water	Weigh Cells
Bleed-Off Gas	Gas Meter + Chromatographic Analysis
Naphtha Scrubber Reactivator Gas	McAfee Gauge + Chromatographic Analysis
Amine Scrubber Reactivator Gas	McAfee Gauge + Chromatographic Analysis
Debutanizer Overhead Gas	Gas Meter + Chromatographic Analysis
Chromatograph Purge Gas	Gas Meter + Chromatographic Analysis
Compressor Leak Gas	Nitrogen Content

Weight and elemental balances are performed; elemental analyses are done by adjusting H_2O , etc., so that elemental balances are good to a couple of percent for 5-7 days; larger variations may be observed on individual days. "Settling" in the lines had been eliminated by not using tees; all tank contents are stirred.

Table AC-1.2-5 Physical and thermal property data for the SRC-II project.

Coal Liquid Characterization - 50°F Cuts

density

molecular weight

elemental analysis

viscosity

specific heat

heat of vaporization

thermal coefficient of expansion

Heat of Reaction in Dissolver

- data from adiabatic dissolvers in pilot plants
- function of coal type and hydrogen consumption
- consistent method for calculating quench requirements for demonstration plant design conditions

Vapor/Liquid Equilibrium Correlations

Basis: modified Grayson-Streed correlation

- Standard correlation for critical temperatures, critical pressures modified to suit data on coal liquid vapor pressures.
- Experimental data on light gas solubilities (hydrogen and methane), at high P and T, have been incorporated.
- Experimental program for verification of K-value correlations, using representative composite streams from the SRC-II pilot plant (P-99).
 - High-pressure separator conditions:
2000 psia @ 400 to 800°F.
 - Intermediate pressures:
50 to 200 psia @ 500 to 800°F.
 - Vacuum system studies:
15 to 30 mm Hg @ 600 to 750°F.

It is claimed that only small performance differences have been encountered among the three operating SRC-II dissolvers (Merriam, Harmarville, and Ft. Lewis) that cannot be explained by Gulf's reactor model. The gas flow is plug flow, while the liquid-solid slurry is essentially fully back-mixed. The conception of the reaction path is that the first, fast reaction regime must be handled by empirical correlations, with no real handle on the reaction kinetics, whereas good kinetic correlations can be developed for the slower reaction regime that follows. Hold-up relationships have been developed for the gas and slurry phases. There is no evidence of solids settling at the gas velocities used and no detectable change in particle-size distributions in and out of the dissolvers; the demonstration-plant dissolver will use higher velocities and therefore settling is not expected to occur. The particles display a 3 μm median diameter, with a range of 1 to 20 μm . Large inert particles may settle, but means for dealing with this problem are available.

There is a bench-scale, continuous, stirred-tank dissolver, and results from this unit and the three SRC-II dissolvers mentioned above are consistent. These comparisons have served to verify the reactor model to some extent.

There are minimum values for the liquid and gas velocities that must be maintained to preserve thermal stability. More research could be used on this problem.

The Ft. Lewis dissolver is 24 inches in diameter. There are no plans for a full-scale mockup of the demonstration plant dissolver; instead, the reactor model (based, in part, on experiments with mockups at a smaller scale) is being used for this purpose.

A dialog developed over Gulf's desire to use its reactor model for a harder look at operating transients, such as start-up or upsets. Workers at Gulf want to use the model to develop control philosophies: e.g., is it best to

turn down the gas and slurry flows in step with one another or to turn down one of these flows at a faster rate? Gulf would like to develop a simulator that could address such questions and could eventually be used to train SRC-II operating personnel.

D. Modeling of the Preheater

Workers at Gulf believe that they have some feeling for the preheater from using kinetics for the fast reaction regime in this unit. However, research is clearly needed to obtain a tighter handle on preheater design and operation. The demo plant will use a short-residence-time preheater. Ft. Lewis personnel will operate such a preheater at some time in the future. Ft. Lewis is not the proper place to study the fundamentals of the preheater: it will give an overview, but other work should be done on a smaller scale.

There are plans to study flow regimes in the preheater and in the reactor effluent line. DOE has agreed to fund this work at the technical level, and the matter is now in DOE procurement. It is hoped that "homogeneous" flow can be achieved in the preheater, i.e., the so-called bubble/froth regime will obtain with a well-dispersed liquid phase.

E. Comments on the SRC-II Development Plan

It appears that some of the Gulf engineers are not totally satisfied with current SRC-II development plans. Some of the Gulf people would modify Ft. Lewis to conform to the flowsheet now contemplated for the demo plant and would obtain data from Ft. Lewis operating in this mode in time to modify the demo plant design. [Scoping studies of the recommended Fort Lewis modification became later (February 1980) a part of the SRC-II demonstration project.]

The "design coal" for the demo plant is a "Panhandle Coal", meaning a range of coals from the West Virginia Panhandle, with enough flexibility in the demo plant design to handle a range of these coals. A group of FERWG members, who visited Ft. Lewis last May, was struck by the variability in performance on a number of Pittsburgh Seam coals. When asked about the extreme difference in behavior, for example, between Blacksville and Powhatan coals during the Harmarville visit, Gulf personnel stated that the Blacksville coal "has an ingredient missing", but further information was withheld because Gulf has filed a patent application on this. It is likely that Gulf personnel know how to "treat" the Blacksville coal or to add something to make it perform better; however, there does not yet appear to be a handle on the economics of "upgrading" Blacksville coal in this way. Blacksville coal can be made to perform as well as Powhatan by operating at higher reaction severity (higher pressure and temperature). The tenor of the discussion of the poor performance of Blacksville coal, in comparison with Powhatan, suggested that Gulf workers are still deciding how to deal with the Blacksville coal most economically. Extensive reserves of the Powhatan type coal exist that are sufficient to support the demonstration plant and several commercial plants using Pittsburgh Seam coal.

Another element of uncertainty is the gasification of vacuum bottoms by the Texaco process. Only limited test data are available for operation of the Texaco process on liquefaction bottoms. It might fairly be questioned whether the data base for this process is sufficient for confident design of the demo plant at this time.

F. Process Research

Most of the needed process studies are in progress, either at Gulf or at PETC. The following additional investigations may be useful:

a. Coal Effects -- Most of the research to date has been done on Kentucky and Pittsburgh Seam coals. Identification of effects produced by coal-ash constituents, added pyrites and catalysts on a broader range of coals would be helpful to a future industry.

b. Solvent Effects -- The observation that the solvent has the same composition in and out of the reactor does not rule out significant solvent effects in the process but could reflect on a particular steady-state that is achieved during processing.

c. Control Strategies -- Modeling and simulation to plan control strategies for transients and system perturbations should be done as soon as possible and were suggested by Gulf personnel.

d. Reactor Design -- The proposed modeling and tracer studies were well thought out.

e. The PDU P-99 is a well designed, small unit which, based on a record of over 40 runs since 1976, has supplied useful process data with only modest operational problems. Problems with letdown valve life, preheater designs scale-up, etc., have been common to all of the coal-liquefaction units. Mention of an actual failure due to chloride stress-corrosion cracking of a line is a warning on possible materials problems that must be understood and considered in any scale-up design. A great deal of additional information on the SRC-II process could be obtained with the PDU P-99, particularly evaluations of a broader range of coals or even coals from the same seam but different mines or locations in a mine. An adequate range of operating variables has been covered to support the demonstration plant design.

The PDU P-99 dissolver has an L/D of about 20, the plant at Ft. Lewis of about 15, and the demonstration-plant design about 10. If PDU P-99 is substantially backmixed, the demonstration plant will be even more strongly backmixed.

The ability to obtain good material balances and sustained steady-state operations indicates good design practices. The data base on the coals tested (Kentucky and Pittsburgh Seam coal) should be sound.

G. Basic Research on Modeling and Scaling

For reasons that are unclear to us, we have encountered educated opinion to the effect that "scale-up of coal liquefaction plants represents no problem and research is not needed in this area." This judgement is further emphasized by the existence of systematic studies at university laboratories on modeling and scaling of coal-gasification systems (largely supported by EPRI), whereas comparable basic studies on modeling and scaling of coal liquefaction units do not exist. While coal-gasification plants are being scaled by about a factor of 10, coal-liquefaction plants are being scaled by more than a factor of 100 in proceeding toward commercial plant sizes.

FERWG and Gulf Oil Co. participants at the discussions of the SRC-II pilot-plant and demonstration-plant program on October 21 concurred that a substantial, well integrated, and sound program on modeling and scaling of coal-liquefaction processes is of the utmost importance and should be viewed as a small incremental charge for increasing the probability of success of the SRC-II demonstration plant. Studies of this type will furthermore assist in the development of logical process-modification procedures in the event that unexpected operating difficulties are encountered.

The motivation for the recommendation made in the preceding paragraph will now be clarified.

The normal progression of complex process technology, performed in industrial laboratories and funded by discretionary company resources, involves a meticulous progression of size from bench scale to the small pilot plant and then to progressively larger process development units before a demonstration module is constructed. There are no fixed rules for the measures of scale up. Instead, depending on the process under development and the operating difficulties encountered at each scale, intelligent judgements are made on how to proceed in view of acceptable risks at the needed levels of investment. This widely accepted procedure is being short-circuited because of (a) economic and political pressures for early demonstration of successful operation and (b) the

infusion of very large amounts of government money that reduce or eliminate the risk of failure for the operating company. Both the SRC-II and H-coal demonstration plants are being scaled up more rapidly than they would be scaled up without government support.

Accepting the decisions on funding and scale-up that have already been taken, it clearly falls within the FERWG charter to seek supporting R and D activities that will reduce the risks of failure in these costly programs. While our fundamental knowledge of procedures for modeling and scaling is adequate, it is clear that the available methods cannot be applied without learning about process performance and variables that must be defined empirically. What is the set of dimensionless groups that must remain invariant for "exact" scaling? Which of these dimensionless groups (Peclet, Reynolds, Damköhler, etc. numbers) are of primary and which of secondary importance? What are the proper constitutive equations for the non-Newtonian fluids that represent coal slurries? What kinds of physical measurements are needed on properties for a detailed modeling study?

We were gratified to find at the Gulf Research and Development Corporation a group of dedicated people who were asking questions of the type specified in the preceding paragraph. We strongly support their proposals for an augmented effort on modeling and scaling within the active research group that is responsible for the development of the SRC-II demonstration plant. In addition, we recommend the development of a longer-term, university-based program on the general problems of modeling and scaling of coal-liquefaction components and processes, coupled with systematic measurements of those special physical and chemical properties that must be known to improve the process descriptions provided by models and the probabilities of successful scale-up.

Studies on modeling and scaling are not right or wrong. They are either useful or useless. We expect that they may prove to be useful in increasing the successful and cost-effective development of SRC-II demonstration plants for coal liquefaction.

AC-2. REPORT OF FERWG SITE VISIT TO
EXXON RESEARCH AND ENGINEERING COMPANY,
BAYTOWN RESEARCH AND DEVELOPMENT DIVISION
BAYTOWN, TEXAS
(JULY 13, 1979)

FERWG Members Who Participated: John Clardy, L. E. Furlong (host),
S. S. Penner, A. M. Squires, and J. R. Thomas.

EXXON Participants: R. F. Bauman (Director, EDS Process Research Laboratory),
L. E. Furlong (Director, Coal Research Laboratory), W. N. Mitchell (Section
Head, EDS Process Research Laboratory), R. P. Souther (Process Superin-
tendent, ECLP-Carter Oil), S. Zaczepinski (Section Head, EDS Process
Research Laboratory).
R. C. Neavel (Scientific Advisor) joined the group for discussions during the
afternoon and L. L. Ansell (Project Leader for CLPP) served as a guide at CLPP.

A. Facilities and Status of the Exxon Donor Solvent (EDS) Process

The following facilities are currently available or under consideration at
Baytown:

- (a) A tubing bomb reactor, which is a batch autoclave for the liquefaction of samples amounting to several grams of coal in a donor solvent and under an atmosphere of hydrogen; also a stirred autoclave for liquefaction of larger coal samples (30 g) in a donor solvent under H_2 pressure.
- (b) RCLU (for Recycle Coal Liquefaction Unit), which is a flow system for isothermal reaction of coal at a rate of 50 and 100 pounds per day. The solvent is recycled while the hydrogen flow passes once through the RCLU; there are two RCLUs at Baytown.
- (c) CLPP, pronounced clip (for Coal Liquefaction Pilot Plant), which is a complete unit for the liquefaction of one ton per day of coal. Both hydrogen gas and solvent are recycled. The reactor is approximately

adiabatic. There is a vacuum pipe still giving a 1000° F cut point.

(d) ECLP, pronounced eeclip (for EDS Coal Liquefaction Plant). This unit processes 250 tons per day and is sufficiently large to test furnaces, let-down and other valves, pumps, compressors, and other components that may then be readily adapted or scaled for commercial applications. The flow scheme is the same as for CLPP. The ECLP facilities cost $\$110 \times 10^6$ while the program is funded for $\$240 \times 10^6$. A Flexicoker pilot plant is available for use in the Baytown refinery. Modifications are required to run coal liquefaction bottoms. The decision to modify and test this unit is currently being evaluated.

The ECLP is about 1% of full scale insofar as coal-handling capacity is concerned. It is a salutary experience to view the enormity of this operation and to contemplate the prospect that production of 2×10^6 B/D at 60-70% efficiency will require 36 plants, each processing 100 times the amount of coal that will be used in ECLP.

(e) A design basis for a commercial EDS plant processing 25,000 to 30,000 tons per day of coal is expected to be ready for licensing by 1982. A developed bottoms process would also be required.

A CLPP One unit operated at 0.5 ton/day between about 1965 and 1969. CLPP One had centrifuges and filters, as well as a vacuum tower to recover residue-free product. The primary purpose in the operation of CLPP One was to establish the process scheme for the EDS Process. CLPP One was dismantled when Exxon's interest in coal liquefaction waned because of development of Alaskan North Slope oil. CLPP Two, the present unit, was built in 1975. ECLP was designed in 1974-75, but incorporates results of CLPP operations obtained during 1975-78.

The EDS development since September 1977 has been funded through a cooperative agreement. Participants include EPRI, DOE, ARCO, JCLD, Ruhrkohle, Phillips, and Carter Oil. Essentially all of the major pieces of equipment for ECLP are now in place, but piping is not yet complete. ECLP is scheduled to start operation in February 1980.

With the currently envisioned cooperative agreement and assuming sponsor approval of the Flexicoking Part II program, the design basis for a pioneer commercial EDS plant could be established in 1982. Without the Flexicoking component, an acceptable alternative such as partial oxidation of bottoms would require definition. If a large pilot plant program were required for partial oxidation, a design basis might not be available until 1984 or later. Given a design basis in 1982, a commercial plant could be on-stream in 1988 or 1989 at the earliest. This projection assumes that the commercial plant owner would have favorable financial incentives and expeditious assistance on permitting, particularly with respect to environmental and health issues. It would be very difficult to accelerate this schedule at acceptable levels of risk.

As we have already noted, the ECLP (which is one percent of full scale) project is funded at $\$240 \times 10^6$. Exxon had $\$32 \times 10^6$ in the EDS Process before this project was funded jointly. Contributions are coming into the $\$240 \times 10^6$ budget, reducing Exxon's and EPRI's shares. A $\$20 \times 10^6$ contribution earns the right to "bring in a coal" for testing in CLPP and to become a candidate for testing in ECLP as well. The Japan Coal Liquefaction Development Co. has made such a contribution. A $\$5 \times 10^6$ contribution (obtained so far from Phillips, Atlantic Richfield, and Ruhrkohle) earns limited voting rights, access to certain data, and the right to attend all meetings.

B. Process Considerations

The question why German coal liquefaction people persist in using much higher pressures than are used for EDS was discussed. Use of a good donor solvent reduces the effect of increasing H_2 pressure. German coals are apparently harder to liquefy than U.S. coals.

Brief mention was made of the utility of a proprietary "solvent quality index" in processing coal liquids.

CLPP is now operating in a series of tests with recycle of some of the bottoms from the vacuum tower. This procedure returns some heavy liquefied matter to the reactor along with some mineral matter and unreacted carbonaceous residue. Typically, the vacuum bottoms might contain about 25% mineral matter. CLPP was running on July 13 on Monterey Illinois No. 6 coal and will be shifted to another coal in about a week. The next coal will be Pittsburgh Seam coal from the Ireland mine.

There was no opportunity for an extended discussion of the effects seen in the EDS process performance as the result of the recycle of heavy matter. Apparently, R. Bauman (Exxon) believes that the role of the recycle is simply that of shortening the residence time in the liquefaction reactor for the "easy" parts of the coal to liquefy; these yield lighter products that are not recycled except as donor solvent species after hydrotreating. At the same time, the residence time is lengthened for the "hard" parts of the coal, i.e., for the heavy material being recycled. Bauman stated that Exxon has experimented with additions of mineral matter and found little effect if a "good" solvent is used. However, these additions were seen to have beneficial effects when a "poor" solvent was used. **

*The Germans frequently added sodium sulfide to their liquefaction systems (primarily to control chlorine, but incidentally also adding H_2S). Some investigators believe that the addition of the sulfide improved liquefaction performance.

** Results presented at the EPRI Coal Liquefaction Contractors meeting in Palo Alto in early May tend to indicate that some unidentified chemical species in the recycled heavy solubilized matter may serve as excellent "hydrogen shuttles", transferring hydrogen from the gas phase onto coaly matter. Workers on the SRC II Process believe that the buildup of mineral matter in the liquefaction reactor can produce important catalytic effects; this view may not be inconsistent with the Exxon experience reported by Bauman, if Exxon's solvent is of better "quality". A personal communication from Douglas Montgomery to suggests that one result of the buildup of mineral matter and of unreacted residue in a liquefaction reactor is to coat tiny spherules of mesophase with such matter soon after such spherules are formed. The coatings tend to prevent spherules from agglomerating into larger masses leading to harmful accumulations of solid reactor residues and also provide catalytic matter in close proximity to the mesophase to promote its hydrogenation and its "reversal" to solubilized matter.

C. Comments on Equipment

RCLU has a preheater with tubing 1/18 inch in inside diameter. Experience has been good with this preheater and with the 3/8" I.D. tubing used in the preheater of CLPP. The later consists of a coil in a fluidized-bed sand "bath". ECLP will use a fired heater, and the ECLP program includes extensive work on the preheater. *

CLPP has four reactor segments in series, each 25 feet tall and 2.62 inches in inside diameter. The flow is upward in each segment. ECLP will also have four reactors in a similar configuration, each 60 feet tall and 2 feet in inside diameter. These are open reactors without internals. The velocity of flow is about 3 times greater in ECLP than in CLPP; it is about 3 to 4 feet per minute in ECLP.

Exxon has conducted extensive tests of full-scale cold models of the ECLP reactor. Bubble sizes of 2 inches and smaller are contemplated; workers at Exxon believe that the presence of solids in the reactor limits the growth of gas bubbles. Backmixing caused by bubble tracks and eddies is not believed to be a problem. **

Letdown valves have shown service life times of a few days in early CLPP operations. The valves now last for 15 to 30 days. A special tungsten carbide with a minimum of binder is used in these valves: Kennametal 703 with 2% Co-Cr matrix. EPRI is currently sponsoring development work in this area.

ECLP will have block valves so that letdown valves can be changed during the run.

* A long-range possibility is a coal-burning fluidized-bed preheater. The bed would be at atmospheric pressure, and preheater tubes would be housed within the combustion bed.

** It has been noted by several FERWG members that the hydrogen gas flows in the EDS and H-Coal processes are on the order of one third of the hydrogen flow in SRC II, which may lead to easier scale-up for these processes. The larger hydrogen flow in the SRC II reactor, achieved through a larger recycle of gas, is probably necessary to provide a larger hydrogen gas inventory in this reactor.

Vacuum bottoms from the vacuum tower have a residence time at 700° F of about 20 minutes in CLPP. It was noted that some of the viscosity problems experienced in handling vacuum bottoms may possibly be associated with long residence times although Exxon experience, based on tests in which the material was held at 700° F for much longer times, did not lead to problems.

The holdup time of vacuum bottoms at 700° F in ECLP will be 30 to 60 seconds. The bottom of the vacuum tower in ECLP is at an elevation of about 50 feet, and the pump can be situated close to the bottom of the tower. The top of the tower is 130 feet from the ground. The elevation of the tower provides a barometric leg to maintain vacuum and flow in the event of a pump failure.

Vacuum bottoms pumps in CLPP had service lives of a few hours at first. Current experience is a life of about 1 month. The pumps are off-the-shelf models modified by Exxon. Longer pump life is expected in ECLP because it will be possible to purge bearings and seals. Purges cannot be afforded at the scale of CLPP because of the dilution of process material; purges would affect material balances adversely.

Corrosion during fractionation, of the type reported to FERWG at Fort Lewis, has not occurred, presumably because "acids" do not survive the EDS hydrogenation process.

Exxon experience confirms the advice heard from the SRC II process crews: do not allow coal liquids to sit at high temperatures; keep them moving!

D. Facilities Visited

Ansell served as tour leader for the FERWG group to the RCLU and CLPP facilities. Noteworthy is a nitrogen-blanketed set-up for processing coal samples to produce comminuted material at the sizes needed by Exxon's various coal-conversion pilot plants.*

* One of the FERWG members commented on discussions with Whitehurst and others concerning the difficulties encountered when a coal researcher tries to obtain good coal samples that have been protected from oxidation. It would be useful if arrangements could be made for Exxon to distribute samples routinely to a number of qualified "subscribers" whenever a new coal is processed in its coal-preparation system.

Furlong reviewed some of Exxon's gasification research. Exxon uses tiny glass U-tubes for fluidized-bed tests, as well as tiny fixed beds. Exxon's one ton per day pilot plant for catalytic gasification is now in shakedown: the reactor is 10 inches in inside diameter and 80 to 100 feet tall.

Souther showed FERWG members the ECLP facilities. Major equipment is in place, whereas much of the piping still needs to be installed. Coal receiving and preparation occupies a large area but represents only about 10% of the $\$110 \times 10^6$ cost for ECLP. As is usually the case for coal-liquefaction plants, the liquefaction reactors themselves are very small in comparison with the remainder of the equipment. The plant was engineered from a model, and a view of the model provides an excellent impression of the plant to be.

E. The Exxon Flexicoking* Pilot Unit

A Flexicoking pilot unit for 2 barrels per day has been run on coal liquefaction bottoms. ECLP will not have a Flexicoking unit. Plans have been made, but were not discussed on July 13, for larger tests of the Flexicoking of liquefaction bottoms. The "ash" purge from a Flexicoking unit is expected to contain about 5% of the carbon in the liquefaction bottoms fed to the Flexicoking unit. Disposal of this "ash" will require procedures related to those used by boiler operators burning large quantities of coal.

Flexicoking is not viewed as a mandatory component of the EDS project.

F. Public Health Issues

Since coal-derived gasoline components have comparable cut points to those of petroleum-derived gasolines, the concentrations of polynuclear aromatics (PNAs) are also expected to be similar and will thus not introduce new environmental hazards. Heavier fuel oils made from coal are, however, higher

* Flexicoking is an Exxon service mark.

in PNAs than oils made from petroleum; therefore, appropriate testing and perhaps special precautions must be considered, at least for the heavier fuel oils made from coal liquids. The development of proper disposal systems for the "irrevocable" bottoms requires study; perhaps permanent storage in clay-enclosed areas will be acceptable.

G. Research Recommendations

The principal research recommendations are summarized below:

1. Coal-characterization procedures must be developed that define the suitability of coals for liquefaction by a specified conversion process.*
2. Work should be done on the hydrodynamic configurations used in the liquefaction unit, which may well show recirculation and bubbling at full commercial scale. Fluid flows have been studied in hot, three-phase systems; the observed bubble-size limits were about 2 inches.
3. Homogeneous catalytic processes in coal liquefaction should be studied. In this connection, a deeper understanding must be acquired of the chemical processes that occur during coal liquefaction when a recycle is used of a heavy, solubilized substance containing mineral matter (e.g., a vacuum tower bottoms).
4. An urgent practical problem deals with the development of materials and/or designs for better valves, pumps and compressors for use with coal-liquid or residue-liquid slurries. The proper design and construction of long-lived letdown valves has appeared as an especially troublesome problem. Such materials as LT α (developed for heat shields on reentry vehicles), resilient polymers or rubbers should be screened systematically to assess their potential utility in withstanding erosion and corrosion during liquefaction.

* A discrepancy was observed between the performance of Burning Star and Monterey Illinois No. 6 coals. Furlong expressed the view that Exxon's work with Burning Star may not have been sufficiently extensive to define the best processing conditions for the primary coal liquefaction step. Nevertheless, the striking difference in behavior observed for these two coals is a paradox needing study.

5. There is an urgent need to develop a number of instruments for measurements of important process features and controls. These instruments are the same as those identified by workers at the SRC II facility in Fort Lewis. The following important and specialized measurements are not currently being performed successfully or the needed techniques are not available:

- (a) on-line characterizations of slurry concentrations, especially with small density differences between coals and slurries;
- (b) flow measurements for slurries;
- (c) slurry levels and heterogeneous matter distributions in flow channels;
- (d) accurate measurements to define water-oil interfaces, which are now estimated from density differences;
- (e) convenient techniques to define the oxidation states of coals and coal liquids, which are probably not adequately defined by sulfate levels and may change drastically with very small oxygen uptakes;
- (f) development of on-line viscometers to characterize the flows of the non-Newtonian fluids arising in coal-liquid handling;
- (g) design of accurate sensors for line openings and closing.

6. Handling and viscosity estimations for vacuum bottoms represent special problems because of their non-Newtonian rheological properties. What are allowable hold-up times for the bottoms? In CLPP, vacuum-tower separation was accomplished in minutes at $\sim 700^{\circ}\text{F}$ and 25 mm Hg. The "repolymerization" processes which occur are complex, poorly understood, and justify careful chemical research to elucidate the nature of the phenomena.

7. Identification of important problems in scale-up (e.g., proper design of the flushing system or predictions of pump failure), if any. Slurry pumping will become easier for larger units. Flow studies have involved pressure measurements on heptane-nitrogen-coal mixtures (heptane was chosen because it has nearly the same density and viscosity as the liquefaction solvent). Vortex flows have not been observed in the prototype studies whereas solids precipitation (CaCO_3 forming on the walls) is known to occur. Scale-up to commercial plant

size is based on use of the same chemical conversion times that have been found to be acceptable in pilot-plant studies.

8. Are there special problems associated with solvent fractionation and hydrogenation, as was suggested by workers at the SRC II facility? Although the evidence is inconclusive, the Fort Lewis experience may be the result of selection of a "special, highly corrosive cut." In the Exxon experience, fractionation and hydrogenation were directly adapted from petroleum practice.

9. What types of product specifications (e.g., contents of sulfur, nitrogen, etc.) must be met by coal-derived liquids in order to meet current and anticipated future environmental standards?

10. Effective procedures for separating ash from coal liquids should be developed.

H. Coal-Characterization Research

Richard Neavel described a long overdue program "to bring coal science into modern times." This program encompasses several stages: (a) the careful collection and preservation of a large (66) number of U.S. coals that span the usual rank classification; (b) the measurement of a large (unspecified and some proprietary) number of physical and chemical properties of vitrinite-rich samples; (c) rating the performance of these coals in a variety of processes; (d) correlating the measured chemical and physical properties with performance in coal processing. The output is thus a matrix of coal "properties" that will predict performance in liquefaction, pyrolysis, gasification, combustion, or other coal-conversion application. There are no restrictions concerning the "properties" that are not yet recognized to be important. In particular, Neavel concurs with the value of John Larsen's suggestion that the level of some obscure chemical functionality in a coal, ordinarily present in only small amounts, may turn out to be crucial in determining behavior in an application such as coal liquefaction.

An obvious problem in the development of a useful matrix is the failure to measure an important property. An example of this type arose in the discussions which showed that pore-size measurements (which are known to be important in defining combustion behavior) are not currently included in the properties table. Omissions of this type will probably be corrected through the participation of a significant segment of the coal-science community.

A more significant problem is a methodological one. What would a successful outcome of this program be? One outcome stressed by Neavel is the matching of coal to process. It is known in a general way what coals do well in what processes but in detail there are troublesome problems. For example, the relative merits of Monterey and Burning Star (both Illinois No. 6 coals) in the SRC II and EDS processes are probably reversed. Will this type of behavior be predicted with the proposed correlation matrix? If the answer is yes, then a great deal will have been achieved. It is, however, doubtful that the coal-characterization matrix will eliminate the need for fine tuning of coals in process applications.*

An important goal of coal research is the development of leads to new chemistry for processing coal. Speculations and science on the molecular level will be required to create new processes. The connection of the correlation matrix with molecular structure remains as a challenging problem. In a sense, the proposed coal-characterization program is an effort to augment quantitative understanding (which will require decades of detailed work) by well defined empirical tests and empirical knowledge.

*This type of problem is being addressed by focusing research on a close examination and comparison of "coal pairs", one of which is known to perform well in coal liquefaction and one of which is known to be unsatisfactory; Burning Star and Monterey coals provide an example of such a pair. Similar pairs (or trios or quartets) can be identified among other Pittsburgh Seam coals.

AC-3. REPORT ON FERWG SITE VISIT TO HYDROCARBON
RESEARCH, INC., LAWRENCEVILLE, NEW JERSEY
(AUGUST 16, 1979)

The following FERWG members participated in the site visit to Hydrocarbon Research, Inc.: Clardy, Furlong, Leder, Penner, Ross, Sieg, and Squires. The group was joined by Irving Wender of DOE in all of the discussions; he provided valuable comments and advice.

AC-3.1 The H-Coal Process Developed by Hydrocarbon Research, Inc.
(HRI), a Subsidiary of Dynalectron Corp.

The following HRI personnel participated in the discussions:

Dr. P. H. Kydd, Vice President-Technology;
Mr. A. G. Comolli, Director of the Liquefaction Program;
Mr. M. Merdinger, Manager of the Trenton PDU;
Mr. E. Johnson, inventor of the ebullating bed and analyst
of H-Coal process development studies and data;
Mr. M. Chervanek, Assistant Director of the HRI Lawrenceville Research Laboratory.

We are greatly indebted to these experts for technical advice and information. Visual displays used in the presentations have been freely incorporated in this trip report.

The H-Coal process was started in 1964 and has been supported by DOE, EPRI, the Ashland Oil Company, Conoco Coal Development Co., Commonwealth of Kentucky, Mobil Oil Corporation, and the Standard Oil Company of Indiana.

It is patterned after the commercial H-Oil process. Both the H-Coal and H-Oil processes employ ebullating beds (see below) and conventional hydrodesulfurization catalysts (typically, 3% CoO-15% MoO₃ on alumina extrudates). Variants in catalyst formulation have been explored to some extent. The formulation, life, and management of the catalysts are important problem areas for research.

The flows in the 3.5 ton per day process development unit (PDU) are shown schematically in Fig. AC-3.1-1. Test-runs were terminated after 30 days. The H-Coal process contains a two-stage pressure let down from 2750 to 1200 psi and then from 1200 psi to atmospheric pressure, through tungsten carbide let-down valves with service lives of 30-60 days. Improved designs and materials for the construction of let-down valves are important problem areas for research.

Yields of three barrels of oil per ton of coal were reported in the boiler fuel mode. Hydrogen consumption was 4000 SCF/barrel. The products consisted of C₁ - C₄ gases, naphtha, boiler fuel, residue, and ash. The liquids produced are about half in the fuel oil range. Distillates typically contained 0.1-0.2% and the boiler fuel less than 0.5% S. It was reported that 80-90% of the organic sulfur was removed.

Yields from PDU runs in the syncrude mode were reported as follows: C₁-C₄, 8-11%; C₄-400°, 17-19%; 400-650°, 10+%; 650-975°, 8.5+%; 400-975°, up to 29%; 975°+, 20-30%; unconverted coal, 5-7%; ash, 11%. The vacuum bottoms were about 45% solids. Hydrogen additions to liquids are 10% based on liquids or 5% based on coal. The management, supply, and cost of hydrogen for H-Coal plants are primary factors in determining product costs.

Representative process operating conditions and product properties are given as follows: system pressure, 2750 psig; H₂ partial pressure, 1800 psig; reactor temperature, 850°F (intentional temperature excursions up to 880°F were used); space rate or equivalent, 2 wet tons/hr/inventory wet ton; sulfur reduction, 80% of organic and 50% of pyritic sulfur; catalyst make-up rate, 0.3-6 lb/ton

Fig. AC-3.1-1 Schematic diagram showing the PDU flows.

and typically 1 lb/ton; equilibrium catalyst activity, low relative to that of the fresh catalyst; carbon content of the equilibrium catalyst, $\sim 20\%$; solids content of vacuum bottoms, 45-50%; hydrogen consumption, 4000 SCF/bbl when operating in the Illinois No. 6 boiler fuel mode; the PDU reactor temperature control was good; extensive external oil recycle was employed.

FERWG members generally concur with the view that the H-Coal process can be commercialized and that at least the distillate portion of the product may be further processed to transportation fuels using available petroleum-processing technology.

i. The Ebullating-Bed Reactor

The H-Coal process uses a catalytic, ebullating-bed reactor (see Fig. AC-3.1-2) for the initial coal-conversion step. In the ebullating-bed reactor, catalyst pellets are supported by rising flows of hydrogen gas and coal-solvent slurry. The rate of upward flow of the slurry is adjusted by means of a pump that is used to recycle material withdrawn from the top of the vessel and reinjects this same material into the bottom of the reactor. In a commercial-scale H-Coal reactor, the recycle pump will be housed within the bottom of the reactor structure. The recycled material flows downward toward the pump through a down-comer that is situated along the vertical, central axis of the vessel. The primary purpose of the recycle is to maintain proper ebullation of the catalyst bed. Within a well-defined liquid-flow range, efficient mixing occurs and the temperature is relatively uniform throughout the ebullated bed. At the same time, the upper catalyst bed level remains quite distinct. The H-Coal reactor represents a good approximation to the stirred reactor.

EBULLATED BED REACTOR

Fig. AC-3.1-2 Schematic diagram of the ebullated bed reactor.

A key function of the ebullating bed is distribution of the heat load across the reactor. Available operational experience indicates temperature control within $\pm 5^{\circ}\text{F}$ at any given vertical position. The slurry enters the preheater at $250\text{-}300^{\circ}\text{F}$ and is then raised to a design maximum temperature of about 850°F at the reactor exit.

The ebullated bed reactor was developed by HRI and has been used commercially in the H-Oil process. Two commercial H-Oil units have been in operation for 11 years in a refinery in Kuwait; each of these processes 27,500 bbl of oil per day. Another H-Oil unit has been used in a Pemex refinery in Mexico for 6 years and processes 20,000 bbl of oil per day. Thus, the development of the H-Coal process may be viewed as an adaptation of commercial H-Oil technology to coal liquefaction. In Table AC-3.1-1, we summarize the reactor dimensions that have been used or will be used in the development of commercial scale, ebullated-bed reactors.

Table AC-3.1-1 Inside diameters for ebullated-bed reactors at various scales.

Process Scale	Reactor diameter for	
	H-Oil	H-Coal
Bench scale	0.75 inch	0.75 inch
Process development unit (PDU)	8.5 inch.	6 and 8.5 inch.
Pilot plant	4.5 ft	5 ft (at Catlettsburg, Ky.)
Commercial plant	13.5 ft	13.5 ft (projected)

An advantage of the ebullated bed for processing coal, that has been observed by HRI, is absence of formation of reactor deposits of the type observed, for example, by Exxon in its EDS Process. For a properly operating, ebullated bed, incipient deposits that may form on catalyst particles appear to be promptly removed from the particles by turbulent shear flow.

HRI personnel have built a full-scale cold model of the 5-ft. ebullated bed reactor for the Catlettsburg pilot plant (see Table AC-3.1-1) and have used this model to develop proper designs for internal components that will hopefully ensure successful operation of the internal slurry recycle pump. The original design of the inlet at the top of the slurry downcomer was modified to reduce the quantity of hydrogen gas that is entrained by the down-flow of the recycled slurry liquid. Workers at Amoco are conducting analytical studies of cold-flow modeling on the ebullated bed under a DOE contract at the Naperville research laboratories; this work is closely coordinated with HRI activities.

ii. The Slurry Heater

Workers at HRI, as elsewhere, consider the design of a slurry heater to be a critical problem in scale-up. Alternate designs have been developed for Catlettsburg, with the hope that all will work and with the expectation that the multiplicity of designs will provide safety and flexibility in the operation. The H-Coal process uses a preheater temperature well below the reactor temperature. The SRC II and EDS processes require preheating of the slurry stream to temperatures about 100°F higher than are used in the H-Coal process.

iii. The Catalyst

It appears that practically all of the H-Coal work to date has been carried out with a conventional Co/Mo catalyst. Recently, some work has been initiated with Ni/Mo catalysts and molybdenum-supported catalysts. The available results indicate superior performance for these catalysts. Bench-scale development tests have been made on a number of catalysts. These data suggest that significant improvements may be expected in catalyst performance in the H-Coal process, both with respect to selectivity of the desired products and especially with respect to catalyst life.

Catalyst make-up rates fall in the range 0.3 to 6 lb. of catalyst per ton of coal processed, depending on the coal used and the desired product mix. A limited amount of work has been done on regeneration of catalyst activity: 50-60% recovery of catalyst activity was achieved by combustion and, with new materials, there is the promise of doing better.

HRI personnel made a strong recommendation that catalyst research is an area that will yield significant pay-off.

The results were described on two tests (one on Illinois No. 6 coal and one on Wyodak coal) that were intended to illustrate H-Coal performance with an equilibrium catalyst, i. e. with a level of catalytic activity that remains at a time-independent, steady value when catalyst additions are made on a regular schedule from the beginning of the run. Both tests had durations of only 30 days. The short duration of these runs was set by DOE contract monitors in the light of budgetary restraints. All of the participants at the HRI discussions concurred with the view that considerably longer runs would be helpful to prove that the data reflect the performance of an equilibrium catalyst. Since theoretical calculations show that the equilibrium catalyst level will be achieved only shortly before the expiration of 30 days, catalyst studies should be extended to durations of 60-90 days.

iv. Studies of Upsets

The ebullating bed liquid recycle pump has been shut-off abruptly, without the immediate occurrence of serious consequences. In fact, the bed remained operational for at least 12 minutes, thus allowing time for appropriate operator response.

The ebullated bed has been subjected, on a number of occasions, to abrupt cut-off of flows. Each time the bed recovered easily.

On the other hand, sudden removal of the preheater led to serious consequences because a corresponding, sudden increase occurred in viscosity. This result was not anticipated and its discovery amply justifies a program on the

study of upsets. The operating answer to a sudden loss of the preheater is rapid introduction of light oil into the system in order to maintain low slurry viscosity.

Coke formation was not observed after a brief excursion in temperature to $\sim 900^{\circ}\text{F}$.

v. Letdown Valves

The letdown valves are viewed as critical components by workers at HRI and elsewhere. On the whole, HRI personnel appear to be content with the letdown valves now in use in their bench and PDU units. Sparing is provided so that valves can be changed without interrupting a run. Tungsten carbide valves usually last from 30 to 60 days, which is viewed as satisfactory in process development operations by HRI workers.

Recently, two stages of letdown have been installed in the PDU: the first stage covers the range from about 2750 psig to 1200 psig and the second leads to atmospheric pressure. HRI personnel believe that the performance of this two-stage letdown system represents an important operational improvement.

vi. Carbon Dioxide vs. Water as a Product from Low-Rank Coals

The fact was noted that German researchers in coal liquefaction find oxygen from brown coal to be released primarily as carbon dioxide, whereas HRI H-Coal data for Wyodak subbituminous coal show that the oxygen is mainly in the output water. Johanson stated that the initial oxygen-containing product from Wyodak coal is indeed carbon dioxide, but that this is shifted to water under the conditions of the H-Coal reactor.

vii. Effect of Deep Cleaning

HRI workers showed results indicating better performance with deep-cleaned coal (at 6.4% mineral matter) than with run-of-mine coal (at 18% mineral matter). The inference is that the presence of "ash" in the H-Coal reactor is detrimental.

However, this conclusion cannot be drawn with certainty without careful tests, in which the level of mineral matter of relatively constant composition is systematically varied. The run-of-mine coal in the test probably contained a great deal of slate.

lii. Instrumentation of Ebullating Beds

A temperature reading is taken every foot of height in the bed. There is a density monitoring device on liquid recycle to the ebullating pump; this measurement is used to show if hydrogen is entrained in the liquid. A density reading is also taken in the ebullating bed itself.

ix. Progress in the Construction at Catlettsburg

The construction at Catlettsburg has been delayed. Reorganization of the construction-management team has been an essential step in the redirection of this activity. FERWG members have not performed an independent evaluation of past and current activities relating to construction delays, program management and overview, cost overruns, and related potential problem areas.

x. H-Coal Costing

An independent and definitive cost evaluation for H-Coal has not been made by FERWG members.

Replacement of cobalt-molybdenum oxide catalyst at a rate of 0.3 lb per ton of coal processed was estimated by HRI workers to imply a catalyst-replacement cost of about \$0.30 per bbl of oil produced. At the highest quoted catalyst replacement rate of 6.0 lb/per ton of coal processed, catalyst costs with regeneration are substantially less than \$6.00 per bbl of oil produced.

Currently preferred catalyst choices are Amocat Co/Mo and Ni/Mo; the Ni/Mo has performed well in nitrogen reduction while the Co/Mo appears to be the preferred catalyst for lowering viscosity and reducing resin and distillate yields. Neither of these catalysts is totally satisfactory for heteroatom removal and for maintenance of hydrogenation activity.

We were told that the cost of a 70,000 bbl/day plant would be about 1 billion dollars (1978), and that this information was available through the DOE. A report was prepared by the Fluor Corporation for ERDA in March 1976, which has been widely circulated but never officially issued. R. Fischer (DOE) has stated that financial parts of the report are not proprietary but the report was not released. At any rate, figures comparable to those cited to us were available in 1976. If the cost estimates refer to 1975 instead of 1978 financial data, they are out of date. In 1975, projected prices of oil were around \$17-18, based on optimistic assumptions about the process and about the cost of capital. It is likely, based on current costs of capital, coal, construction, etc., that oil from H-Coal will cost \$30-45/bbl.

AC-3.2 Research Recommendations

The near-term and long-term directions of supporting research that are required for efficient implementation of commercial H-Coal processes are clearly defined by the remarks contained in the preceding sections. These recommendations are consistent with the view that the ebullating-bed concept used in the H-Coal process represents an attractive alternative for contacting coal, recycled oil, hydrogen, and catalyst, with low preheat requirements. Our research recommendations are also consistent with the views elaborated in joint discussions involving HRI project personnel.

i. Catalyst Development

Improved results in catalyst performance have been associated with improving the bimodal distribution in the size of pores within the catalyst pellets. Experimental findings clearly indicate that research at much greater depth might pay off.

Optimization of the product slate is difficult, because the economic rules that will be in effect 5, 10, or 15 years from now are simply not known. For this reason, catalyst work should be directed toward finding a number of formulations that lead to slates of preferred products, so that ultimately there will be greater flexibility in the choice of catalysts to allow optimization of products under a variety of given sets of economic rules. Thus, ranges of catalysts are needed with improved hydrogen selectivity.

Improved catalysts are needed with better stability against coking and deactivation. Catalysts are required that function efficiently at significantly lower pressures than are now used in the H-Coal process. The many types of process alternatives and controls, which we seek through optimal catalyst selection, clearly justify long-term, fundamental studies in this field. These studies should not deal exclusively with near-term process improvements. Research areas should include mechanisms of catalyst deactivation and activation, as well as kinetic control through catalysts.

ii. Research to Reduce Hydrogen Consumption

The cost of hydrogen is an important cost component in liquefaction and research to reduce hydrogen consumption is clearly justified. The oxygen contents of the processed coals require hydrogen during liquefaction. Therefore, pretreatment of the coal to remove oxygen may become an attractive step. Ideas for pretreating coal to reduce oxygen content should be explored.

In a broader context, we conclude that coal chemistry directed at understanding mechanisms and rates of bond rupture clearly bears on the development of efficient processes for oxygen removal during coal pretreatment, on hydrogen requirements in the H-Coal process, and hence on a dominant cost item in H-Coal technology.

iii. Process Optimization: Instrumentation, Analysis, Process Control, and Modeling

Greatly improved instrumentation is needed for efficient process control and for proper analysis of operating conditions. Tight material balances are an essential component of efficient process technologies and clearly require careful and adequate instrumentation.

The current choice of operating conditions is probably non-optimal and may be responsible, in part, for rapid catalyst deactivation and high hydrogen consumption through cracking and ring-opening reactions. The search for improved operating conditions will require very close coupling between carefully instrumentated operating units and modeling of hot-flow reactors, using interactive and iterative techniques in a search for optimization of process variables.

The goal of optimization of process variables leads to the requirement of hot-flow modeling research with adequate consideration of the fluid mechanics in multiphase, reacting, partially or fully stirred, turbulent flow reactors. The numerical aspects of this work will not be meaningful unless they are tied to a measurement program on small- or large-scale units using proper instrumentation to measure those process variables which are shown to be of dominant importance in the modeling studies.

iv. Materials Problems

Pressure let-down valves have been found to have short service lives in the H-Coal, as well as in other liquefaction processes. Short service lives are the result of erosion and of chemical attacks under the operating conditions that are used in practice. The best available let-down valves are Hammel-Dahl angle valves with tungsten carbide seats. These have been found to have service lives of 1-2 months in the PDU.

Material problems with let-down valves will be encountered whenever slurries of coal products are handled in flow systems, especially at elevated temperatures. We recommend a broadly-based program that is designed to define the relative roles of erosion and of chemical attack in these valves, coupled with materials-development research designed to handle inlet and outlet slurries for much longer periods of time than is now possible. In this connection, a careful look at the performance of reentry heat-shield materials (e.g., LT α) may be justified.

In the H-Coal process, the problem of hydroclone erosion appears to have been solved by the use of ceramic hydroclones and proper flow control. This observation indicates the importance of defining the relative roles played by physical and by chemical processes during erosion.

v. Instrumentation for Process Operation

As for other coal-liquefaction processes, instrumentation development to measure slurry flows is needed.

vi. Studies on Reactant Rheology

The extreme temperature sensitivity of viscosity observed during preheat failure in the PDU has been noted. The operational solution of rapid oil injection may well be acceptable. Systematic studies on process upsets should be continued. At the same time, a broadly based research program should be defined in order to minimize the number of surprises that may be encountered during designed and unintentional process upsets.

In connection with reports on earlier site visits, we noted both the complexity and lack of knowledge concerning the rheological properties of coal-slurry flows, which behave as non-Newtonian fluids. It is worthwhile to extend these studies to examination of rheological properties of the reactant, multi-phase mixtures under the conditions encountered in ebullating beds. In particular, viscosity measurements as functions of temperature and pressure should be made for wide ranges of hydrogen flows, a variety of catalysts, and a representative range of coal types.

AC-4. SITE VISIT (OCTOBER 21, 1979) TO THE CONOCO
PROCESS DEVELOPMENT UNIT (PDU)
FOR COAL LIQUEFACTION USING ZnCl_2

The following FERWG members participated in the site visit to the Conoco Coal Development Company (CCDC) at Library, Pa.: Clardy, Furlong, Penner, Reichl, Ross, Sieg, and Squires. The group was joined by I. Wender (Fossil Energy) and R. H. Kropschot (Office of Basic Energy Sciences) of DOE and by R. F. Bauman (Exxon, Baytown). Personnel from CCDC included J. D. Sudbury, R. T. Struck, M. Pell, C. W. Zielke, and others.

A. Process Description

Figures AC-4-1a and AC-4-1b show simplified flow diagrams for the ZnCl_2 PDU. Table AC-4-1 contains a summary of the development process; Table AC-4-2 shows the project goals.

B. FERWG Observations on the Conoco Program

The difficulties that have been encountered with the ZnCl_2 process are readily traced to the following features of the process:

1. It is an innovative process using methods and techniques that are different from those applied in other coal-liquefaction technologies. The presence of molten and gaseous ZnCl_2 and of its derivative compounds dominates every step of the operating procedure and demands the utilization of components that are suitable for handling materials of this type.

Fig. AC-4-1a Simplified flow diagram of the zinc chloride PDU.

Fig. AC-4-1b Simplified flow diagram of the zinc chloride PDU.

Table AC-4-1 Highlights of the zinc chloride process development.

AC-59

1963-1967 CONSOL COAL (CONOCO COAL) UNDER OCR CONTRACT (1.4 MM \$)

- DEVELOPED CONCEPT OF MOLTEN ZINC HALIDE AS A CATALYST FOR LIQUEFACTION OF COAL AND COAL EXTRACTS.
- DEMONSTRATED CONTINUOUS HYDROCRACKING WITH COAL EXTRACT AND $ZnCl_2$ IN A 2 LB/HR UNIT.
- BATCH TESTS WITH COAL FEED.
- TESTED SOLVENT SEPARATION TECHNIQUES FOR CATALYST REGENERATION. DEVELOPED A UNIQUE COMBUSTION PROCESS FOR CATALYST REGENERATION.
- DEMONSTRATED CONTINUOUS CATALYST REGENERATION IN 5 LB/HR CONTINUOUS COMBUSTION UNIT.

1968-1974 CONOCO COAL CONTINUED WORK ON OWN (0.4 MM \$)

- SHOWED PROCESS APPLICABLE TO ALL TYPES OF COAL.
- CONTINUOUSLY REGENERATED SIMULATED SPENT CATALYST FROM COAL LIQUEFACTION AND SHOWED THAT HYDROLYSIS OF $ZnCl_2$ COULD BE CONTROLLED BY ADDING HCl TO THE FEED AIR.

1975-1979 DoE CONTRACT WITH CONOCO AND SHELL

- CONTRACT PERIOD: JANUARY 1975 TO MAY 31, 1980
- TOTAL FUNDING: \$11,410,413

DoE	90%
CONOCO	5%
SHELL	5%

Table AC-4-2 Goals of the zinc chloride project for development of the molten zinc chloride process for the production of gasoline from coal.

I. IN CONTINUOUS BENCH UNITS

- Demonstrate feeding of coal to the molten bed
- Demonstrate high yields of distillate fuels
- Define reaction kinetics and develop reaction model
- In catalyst regeneration, demonstrate high recovery of ZnCl_2 with high removal of N, O, S, and coal ash
- Test materials of construction

II. DESIGN, CONSTRUCT, AND OPERATE A 100 LB/H PDU TO

- Demonstrate operability and equipment reliability with recycle of the catalyst and hydrocarbons
(An integrated run of at least 7 days)
- Demonstrate high recovery of ZnCl_2 in regeneration
- Define suitable materials of construction
- Test alternate reactor designs
- Test methods of achieving low-C spent melts
- Test novel methods for absorbing HCl from gases
- Define all effluent streams from environmental viewpoint

III. CONDUCT ECONOMIC STUDIES TO GUIDE DEVELOPMENT AND
EVALUATE COMMERCIAL POTENTIAL

IV. SUPPORTING LABORATORY AND PATENT ACTIVITIES AS NEEDED

The products formed have very desirable properties (they correspond to high yields of unleaded, high-octane gasoline and smaller amounts of LNG or LPG) and are usable with little further processing. The ZnCl_2 - procedure may well be applicable to a wide variety of coals. Heteroatoms are preferentially removed. Cost projections by Conoco (~ \$0.76 per gallon of gasoline) are favorable but may also be optimistic.

2. The difficulties of the process were apparently not fully appreciated, and the PDU was underfunded and/or underdesigned.

3. The lack of adequate financial support, in turn, has led to deficiencies in each of the following categories: (i) process design with reasonable redundancies; (ii) component developments suitable for handling the fluids at all stages of the process; (iii) adequate research to address fundamental problems, especially in the materials and chemical sciences; (iv) development and installation of adequate instrumentation and diagnostic procedures for process monitoring and control.

C. Observations on Process Experience

Bench-scale runs at 2-5 lbs/hr have produced a high quality naphtha, comparable to unleaded gasoline, in reasonable yields.

The process is based on the fact that zinc chloride will "catalyze" the hydrocracking of coal to single ring aromatics. The used melt, with zinc chloride partly converted to zinc oxide and sulfide and containing also residual hydrocarbons, can be treated with air and HCl at high temperatures (e. g., 1600-1900° F) to allow distillation of pure zinc chloride from the regenerator.

The process has been tested primarily on solvent refined coal. However, Conoco has run enough other coals through the reactor to claim that it is versatile and will accept a wide variety of coals. The coal is fed to the reactor in roughly one-to-one proportion with zinc chloride. The reactor temperature is around 700-800° F while hydrogen pressures varied between 2000 and 3500 psi. Yields of 75% distillate, based on coal (MAF) to the reactor, have been reported; this yield estimate does not include coal required to make hydrogen. Hydrogen consumption of 6-8% (based on feed coal) has been reported.

The significant fact is that two-thirds of the distillate produced is C_5 -200° C, which makes it suitable for facile conversion to gasoline. By comparison, SRC II and EDS consume 5% and 4% of hydrogen, respectively, based on coal feed to the reactor. But only 48% and 34% of the respective product yields are in the distillate range, while still smaller fractions are in the gasoline range.

Catalyst losses were estimated at about a pound per barrel. This loss seems acceptable considering that zinc sells for about 40-50¢/lb. The corrosion-resistant materials of construction used are Inconel 600 and hastaloy.

The nitrogen and sulfur contents of the products are quite low. For example, 3.5 ppm S and 6.6 ppm of N in the naphtha to 400 ppm S and 150 ppm N in the resid are reported. Comparable S and N figures for H-coal and SRC are 100 times higher.

Problems which have been reported relate to the stirrer configuration, long-term corrosion, valve life, and optimization of materials. Workers at Conoco have properly emphasized the need to run the PDU for long times to facilitate estimations of corrosion data, steady-state product outputs, and general problem identifications.

Chemical mechanisms are not well understood. Carbonium ion mechanisms were proposed and ring protonation was hypothesized, but there seems to be no clear corroboration for these views. Furthermore, the precise role of hydrogen, its impact on forward rates, carbonium ion concentration, side reactions, and melt life are all unstudied.

Obvious questions are the following: How low can the hydrogen pressure be before coking sets in? What is the minimum residence time in the reactor? What is the impact of water vapor on yield, melt life, reaction kinetics? Can new rate promoters be found, e. g., BF_3 ?

D. Chemical Problems

The problems encountered in the ZnCl_2 conversion of coal all seem to arise from the novelty of the process. Specifically, how does one move molten and fairly viscous ZnCl_2 solutions around and avoid corrosion and galling? Obvious chemical problems concern regeneration of ZnCl_2 and the related problem of what to do with SO_2 .

Some of the operating difficulties appear to be traceable to the lack of quantitative and qualitative understanding of the chemical processes that occur. A possible model for the " ZnCl_2 -catalyzed" conversion of coal is that it is related to work done at Exxon by M. Siskin [J. Amer. Chem. Soc. 94, 3641 (1974)]. Siskin showed that benzene in very strong Lewis acids ($\text{TaF}_5\text{-HF}$) could be reduced by molecular H_2 . A suggested mechanism involves abstraction of a hydride ion from molecular hydrogen by a carbonium ion. This step would be a crucial distinction between the ZnCl_2 conversion and other processes. There is also a plausible related model in which molten ZnCl_2 does not serve as a Lewis acid but rather as a Bronsted acid. The H_2O , alcohols, phenols, etc., could generate very strong acid solutions which generate carbonium ions for reduction by hydrogen.

The conversion process is remarkably selective and no explanations have been given about what the selectivity is based on. One of our members noticed that the relatively low observed gas yields, especially of butane, impugn the hypothesis that hydrocracking is the basic mechanism in coal conversion using ZnCl_2 .

The inorganic chemistry involved in regenerating ZnCl_2 seems to be reasonably well understood but may well turn out to be more complex than is now believed to be the case. The approach to regeneration appears to be sound.

While we are impressed with the quoted recovery yields of 99.7%, we note that this performance has not been adequately demonstrated on a steady-state basis.

Physical properties (e. g., viscosities) of coal- H_2 - ZnCl_2 mixtures should be measured. The solubilities of different components may be partly responsible for some selectivity in coal hydrogenation.

E. Program Recommendations

We believe that the areas of R and D represented by the ZnCl_2 process are important. In order to make progress in this area, the attractive and innovative technology involved must be pursued in an imaginative and inventive fashion, including work on the fundamental chemistry.

Significant information may be obtained from bench-scale tests, provided that these are carefully integrated with supporting research and analysis. Generally, FERWG members believe that this process would profit from augmented research performed by a cooperating university group.

We regard the Conoco pilot-plant housekeeping as excellent. We view the program difficulties that have been encountered as reflecting technical and engineering difficulties, as well as the lack of adequate research support, which is especially important for new and innovative technologies.

F. Historical Comment on the ZnCl_2 Process

Hydrogenation of coal is nearly 100 years old as a laboratory curiosity and some 50 years old as a commercial reality. The step from the former to the latter was blocked until a satisfactory catalyst could be found. The early history and basic contribution of the developer (I. G. Farben) is expertly summarized in the monograph by W. Krönig: "Catalytic Pressure Hydrogenation". Krönig notes that separation of the process into two steps (liquid-phase hydrogenation followed by vapor-phase hydrocracking) made commercialization possible in the first place; the second-key development was the discovery of sulfur-resistant catalysts.

In the first step, disposable catalyst is used, which is discarded with the ash (while some 90% of the organic coal substance is converted to a vaporizable

oil and some gas). These disposable catalysts (usually tin or iron) are only marginally effective and, therefore, recourse was taken to some drastic operating conditions: 3,500 to 10,000 psi pressure.

The feed to the second step is ash- and metal-free; more effective catalysts could be used in bulk (usually tungsten sulfide is employed on various supports). The product from this second step, the vapor-phase, was effectively cracked down to the motor fuel boiling range.

In spite of major efforts, no significantly different catalysts for coal hydrogenation were developed for about thirty years; the same catalysts were still used in the Bureau of Mines pilot plant at Louisiana, Mo., in 1950. In the interim, the U.S. petroleum industry successfully commercialized the large scale use of supported cobalt-molybdenum catalysts for hydrocracking and hydrofixing of petroleum. When interest in coal liquefaction grew again in the U.S., these catalysts were applied to the processing of coal and coal extract. Developments sponsored by DOE now cover various systems, either based on the old I. G. Farben disposable catalysts (iron, etc.) or based on cobalt-molybdenum catalysts in a variety of configurations (circulation of donor solvent, ebullating beds, and combinations of these two). All four of the major hydroprojects are single-step systems operating at similar pressures (1,700 - 2,000 psi) and, as would be expected, their product distribution differs substantially from the old I. G. Farben sump-phase by a greatly reduced yield of vaporizable product (about 1/2 of the feed-coal); work-up of the residues is, thus, a major processing step.

Using a different version of the German sump-phase, CCDC had concentrated on a two-stage liquefaction concept, which lowered the severity of the first step to a point where no vaporizable product results, thus permitting operation at less than 500 psi while completely eliminating the need for gaseous hydrogen (only donor solvent is used). The resulting heavy liquid (extract) is separated by hydroclones and is then hydrocracked over cobalt-molybdenum catalysts in an ebullating bed (H-Oil process) at appropriately severe conditions, depending on the desired product boiling range.

The purpose of the foregoing comments is to show that workers on hydrogenation of coal have never been able to get around the limitations imposed on processing by inherent constraints. This observation applies to both disposable or heterogenous catalysts requiring fairly "clean" feedstock, in spite of very large efforts over many decades to get around this hurdle.

The use of molten zinc chloride was originated by Everett Gorin at CCDC about 15 years ago and opened the door to an entirely different approach. With this reagent/catalyst, it is possible to convert coal (even some of the less reactive varieties) at the H_2 -pressure levels currently favored in one single step to high quality motor fuel. The conversion is amazingly selective, the yield of CH_4 is substantially lower than that obtained by other catalysts and the boiling range is "narrow" by comparison; there is effectively no residual fuel oil to dispose of. It should be noted that we are dealing with a single-stage process. If one were to list the optimum results desired from a coal-hydrogenation catalyst, one would describe those obtained with molten $ZnCl_2$.

In chemical terms, $ZnCl_2$ permits the direct conversion of the notoriously complex coal molecule to a mixture of single-ring aromatics plus isoparaffins in over 70% yield, based on MAF coal.

One of the interesting aspects of the process is the apparent suppression of carcinogens in the product. This is not a minor consideration, given the findings of various laboratories regarding the high level of apparent carcinogens in the liquids resulting from virtually all hydrogenation processes currently developed by DOE. In contrast, recent tests at MIT have shown that the $ZnCl_2$ -naphtha has virtually the same lack of any significant mutagenic activity as, for example, Amoco unleaded gasoline. Given the great concern about carcinogens, this finding alone warrants real interest in this reaction.

1. The Drawbacks

One difficulty, recognized immediately and the subject of concentrated attention, is the nearly quantitative reaction of $ZnCl_2$ with the hetero-atoms in the coal (O, N, S), which requires the continuous regeneration of the melt. In

principle, this is achieved by atmospheric pressure flash-distillation of the clean ZnCl_2 (it boils at 1,300° F). In a fluid sandbed, the heat is furnished by burning the 6-8% of unconverted coal, which remains in the spent melt, with air. At the same time, the O, N, and S compounds of Zn are reconverted to ZnCl_2 , H_2O , N_2 , and SO_2 . This procedure was worked out to minimize the losses of zinc.

The other difficulty is the corrosive nature of the system, which calls for special materials (Incolay in particular) and the inherent difficulty of handling a molten salt (ZnCl_2 melts at 590° F); this difficulty is particularly severe when operating at the small scale of bench tests or even at the PDU level, a fact which has admittedly not been properly weighed by CCDC.

2. The Effort to Date

The ZnCl_2 reaction was studied with both coal and coal extract as feed on bench-scale continuous equipment, as was also melt regeneration; the initial effort was sponsored by OCR (now DOE); \$1.4 million were spent over three years. This program was followed by further R&D, mostly on catalyst regeneration; \$0.4 million was spent by CCDC on this phase. In 1975, ERDA (now DOE) contracted to explore the process on the PDU scale (1 ton/day). A total of \$11.5 million were spent during the next five years.

After a reconfirmation of the basic concept, the PDU was approved and this has been the main effort since 1977.

The system presented a whole series of new mechanical problems and considerable time was lost before the hydrogenation and the regeneration could finally be tested. Up to this time, the basic hydrogenation reaction had never failed to yield the products and product quality, which made the system exciting in the first place. The mechanics leave a great deal to be desired; the existing hydro-reactor uses stirrers to assure contact between gas and melt, and agitation with H_2 -gas alone (sparging) would be desirable. Insofar as it is possible to tell, there exist no problems which appear beyond correction by improved engineering and adequate supporting research.

In summary then, for about \$14 million spent to date, the door has been opened to a fundamentally novel type of hydrogenation system, which offers evident advantages over the known art.

Economic appraisals based on the small available data base are not very useful, but several studies which were completed all suggested some advantages compared with other multi-stage hydrogenation systems producing equivalent products.

AC-5. COMMENTS ON THE
DOW COAL-LIQUEFACTION PROGRAM
(NOVEMBER 19, 1979)

A review of the Dow coal-liquefaction program was presented at the UCSD Energy Center in La Jolla to the following FERWG members: Clardy, Furlong, Penner, Ross, Sieg, and Squires. Dr. I. Wender of DOE participated in the presentations and discussions. The presentations were made by V. May and N. Moll, who were accompanied by G. A. Klumb, Jr.

The Dow program dates back to 1973-74 when feasibility studies were performed on the processing of coal-derived oils. Initiation of coal-liquefaction development dates back to 1974. During the period 1974-78, work was performed in a miniplant, utilizing first 0.1 lb of coal per hour and then 1 lb of coal per hour. The largest unit that has been operated thus far processed 10 lbs of coal per hour. Actual experimental work was terminated in 1978. A program plan for substantial scale-up was developed during 1979, at which time both process patents and research reports were issued.

All of the work done with the Dow process involved liquefaction of Pittsburgh #8 coal (which contains about 3.5% of sulfur). The process configuration, catalyst description, product output, process variables, costing, etc. were clearly defined in handouts provided by the Dow group.

Compared with the major DOE-supported programs on coal liquefaction, this process shows two novel and potentially important and useful features involving the catalyst feed and the deasphalting system.

A. The Dow Catalyst

The Dow catalyst is a molybdenum compound. The active species formed from the catalyst feed, which is added to the slurry at a level of about 100 ppm of Mo,

is probably $\text{Mo}_{1-x}\text{S}_2$. Compounds of this type are known to be good catalysts, as has been shown by Weiss (University of Munich) and others.

The procedure used to feed the catalyst to the liquefaction unit is a novel one. Thus, a water-soluble molybdenum compound [e.g., $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] is emulsified with the slurry oil and this emulsion is then added to the coal-feed stream. The ultimate particle size of the catalyst was not defined for FERWG but is probably below about one micron with composition close to MoS_2 . The catalyst works effectively although the final product slate involves relatively large amounts of gas, perhaps because of the high operating temperatures ($\sim 470^\circ\text{C}$) used.

The catalyst cost has been estimated to be about \$0.75 per barrel of oil produced. This cost may be decreased if the molybdenum is recovered from the ash (which has been classified as a good grade molybdenum ore) and proper credit is allowed for this metal recovery.

The catalyst is apparently effective in desulfurization but not in denitrification of the feed coal. FERWG members regard it as likely that the molybdenum catalyst will prove to be effective in the liquefaction of a wide variety of coals. The question of catalyst efficacy for coals with greatly different sulfur contents should be carefully investigated under steady-state operating conditions. Research to identify the active catalyst species and its performance with model compounds should also be carried out.

B. The Dow Deasphalting Unit

The very small deasphalting unit (with a three inch diameter) used in the Dow program has performed quite acceptably. A solvent deasphalting procedure is employed to produce a concentrate of mineral matter and unreacted solid in a highly asphaltic liquid; this concentrate may be gasified (e.g., by the Texaco process) to fuel gas, H_2 , or both. The precise nature of the physico-chemical processes occurring in the deasphalting unit (Marangoni effect) may require

elucidation. If the deasphalting unit works as well on a large scale as on a small scale, the workers at Dow will have made a major contribution to the development of improved coal-liquefaction technologies by identifying a new route and reducing the costs associated with solids-liquids separation.

The Dow claims concerning performance of the deasphalting unit should be speedily verified. Does this procedure really pull out heavy, oil-soluble compounds that cannot be readily distilled out under vacuum?

Scale-up of the Dow deasphalting unit should be regarded as a high-priority development item.

C. Process Implications

The Dow process uses a hydroclone to effect crude separation upstream of the deasphalting unit. About 75% of the recycle oil comes from the hydroclone. There is evidence from other work that this type of procedure is beneficial. Thus, the view that this recycle material, as well as some of the heavier oils recovered from the deasphalting unit, have special donor-solvent capabilities is consistent with the observation that the Kerr-McGee supercritical gas-extraction technique for separating vacuum bottoms into an organic phase and a solid residue yields an organic phase which shows beneficial donor-solvent properties.

The Dow process may offer a desirable fall-back alternative for DOE program managers in case unforeseen problems arise, for example, in connection with the SRC-II plant. Thus, the Dow catalyst could be readily introduced into the SRC-II dissolver in case difficulties are encountered with particular types of coals (such as Western subbituminous coals). Use of the Dow catalyst in the SRC-II process might also lead to more uniform product quality. This presumed potential of the Dow catalyst should, of course, first be carefully assessed in small-scale experiments.

The process scheme used by Dow allows vacuum distillation of deasphalted oil, which thus provides another possible cut for inclusion in the recycle stream used in the coal-slurrying step. Investigations on the laboratory scale to explore the efficiency of recycle mixtures (made up from cuts of hydroclone overhead

plus deasphalted oil plus a vacuum distillate from deasphalted oil) could well yield improved performance for well-defined processing techniques. The definition of promising mixture compositions may then lead to potentially useful alternatives for both the EDS* and SRC-II processes.

*Exxon has recently employed a recycle of vacuum bottoms in a modified EDS liquefaction scheme.

AC-6. COMMENTS ON NUCLEAR PROCESS-
HEAT COMMERCIALIZATION STUDY,
GENERAL ATOMIC COMPANY,
SAN DIEGO, CA 92138
(NOVEMBER 20, 1979)

J. Watson and R. Quade presented a review of the General Atomic (G.A.) program on nuclear process-heat commercialization to the following FERWG members at the UCSD Energy Center in La Jolla: Clardy, Penner, Ross, Sieg, and Squires; I. Wender of DOE also participated in all of the discussions.

A. The High-Temperature (HTGR) and Very High Temperature (VHTR)
Gas-Cooled Reactors

The HTGR and the VHTR have obvious and well documented safety advantages compared with light-water reactors. Their commercialization was, however, delayed until very recent times. Because they entered the utility market during a period of active curtailment of nuclear power in particular and of electricity generation in general, market penetration has been insignificant.

The HTGR and VHTR provide access to core temperatures up to about 950° C. These temperatures are sufficiently high to allow coal processing for liquefaction.* Since 30-40% of the coal energy is normally required for various types of coal-processing steps, nuclear process heat promises improvements of 30-40% in coal-conversion efficiency. As an example (cf. the attached hand-out), the use of nuclear heat in conjunction with the SRC-II process leads to a cost estimate of \$25.20/bbl as compared with \$29.80/bbl for jet fuel under otherwise equivalent assumptions.

* Other reactors do not offer this option. Thus, liquid water reactors are generally limited to about 600° F and molten sodium reactors to about 1200° F. Corrosion problems are severe with boiling water reactors.

We believe that a costing study on the utility of nuclear process heat in coal liquefaction should be performed by a process-engineering group of the type that is normally called upon to perform costing studies of synfuel technologies (Fluor, Bechtel, etc.). If these evaluations turn out to be favorable, a serious reevaluation of U.S. commitments in this field (which were smaller during FY 1978 than those of the F.R.G.) may be appropriate.

AC-7. RESEARCH AT THE CENTRAL RESEARCH
DEPARTMENT OF THE MOBIL RESEARCH AND DEVELOPMENT
COMPANY; MOBIL'S METHANOL-TO-GASOLINE CONVERSION
PROCESS, PAULSBORO, NEW JERSEY (AUGUST 16, 1979)

The following FERWG members participated in the site visit to Mobil: Clardy, Furlong, Leder, Penner, Ross, Sieg, and Squires. I. Wender of DOE also participated with the FERWG members.

A. Research at Mobil

Dr. P. B. Weisz, Manager of Mobil's Central Research Department, presented an introduction which was concerned with the strategy of hydrogen addition for gasification, liquefaction and fuel upgrading.

At Mobil, both M. Farcasiu and D. D. Whitehurst gave short talks on parts of the Mobil program on coal characterization and chemistry. There was little in these talks that was not presented in Whitehurst's very good chapter in Organic Chemistry of Coal (ACS Symposium Series, 1978).

Dr. M. Farcasiu presented a brief review of coal structure, stressing the fact that molecular groups of about 100 atoms with molecular weight of about 600 Daltons are connected by relatively weak bonds (50 to 60 kcal per mole). These bonds begin to scission at about 800° F. The chemical bonds within the molecular group of 100 atoms are stronger, in the range 80 to 100 kcal per mole. The molecular composition of these groups is approximately $C_{49}H_{43}O_{6.4}S_{0.8}$ and there are, on the average, 196 C-C bonds per coal molecule. The main problem which confronts liquefaction and gasification is the selective breaking of these bonds. For that purpose, one has available the variables of temperature, residence time in the reactor, pressure, solvent, and catalyst. There is always competition between thermal and catalytic scission. With high temperature, the selectivity of bond breaking by specific catalysts becomes poor; however, catalytic removal of heteroatoms remains effective. As a general rule, it is best to keep the residence time for thermal rupture of bonds as short as possible.

M. Farcasiu noted that the detailed chemistry presented was done with model compounds and primarily concerned the mechanism of oxygen removal under these conditions. This is a matter of some practical concern since oxygen-containing molecules are believed to be responsible for high viscosity and, in their presence, a relatively greater hydrogen consumption is needed to obtain a liquid product with reasonable viscosity. The work showed that it was possible to deoxygenate oxygenated polycyclic aromatic compounds but essentially impossible to deoxygenate simple phenols. The presumed mechanism involves a hydrogenation-dehydration process. The consequences of this observation for coal are not yet clear and the effect of catalysts on this reaction is deemed a high priority study. Farcasiu also pointed out that there were relatively few thermodynamic data for complex aromatic hydrocarbons and hydrogen at elevated temperatures. The concern is that if the hydrogen partial pressure falls too low, extensive dehydrogenation of alicyclic compounds would take place to give an aromatic char. This char could then coat and deactivate the catalysts. It is not now possible to predict a priori how high the hydrogen partial pressure must be to prevent this process from occurring. Finally, she also commented that N removal was not easily accomplished and further work on the mechanism of this reaction and the effect of catalysts were needed.

D. D. Whitehurst supported the view that the characterization of N functionalities and efficient processes for their removal were the major problem in coal characterization and chemistry. Current techniques for N removal result in excessive gas production. Whitehurst also addressed other outstanding problems in coal characterization and felt that "critical coal characteristics" were poorly understood. Questions such as the "molecular weight" of coal and the degree of polycyclic condensation are still to be answered. Another fruitful area for work he suggested is the proposition that if coal is usefully thought of as a polymer, what is the "monomer"? He did not describe methods to attack these problems in his talk or in private conversation but did feel that new analytical instrumentation would be needed.

Both Whitehurst and Farcasiu felt strongly that coal characterization and chemistry would be better served by "concentrated efforts on selected coals and

the availability of documented samples of these coals." This analysis is identical to that which led to the Exxon program described by R. Neavel at Baytown during a previous site visit.

D. D. Whitehurst discussed problems involved in coal dissolution and transformation. He prefers short residence time thermal solution, followed by more selective hydrogen uptake by catalysis. This procedure requires decoupling of the thermal and catalytic processes, which is different from the approach used in the H-Coal process. Whitehurst listed the following characteristics of catalytic processes:

Process conditions are often too severe.

Both thermal and catalytic reactions occur simultaneously.

Catalysts affect the compositions of both solvent and heavy coal liquids.

Most catalysts now in use were developed for petroleum processing.

There are high levels of metals and coke precursors.

In conclusion, Whitehurst identified the following R/D needs:

- i. Development of new tools and techniques for coal characterization.
- ii. Identification of critical coal characteristics.
- iii. Concentrated effort on selected coals.
- iv. Availability of documented samples from all processes.
- v. Improved utilization of hydrogen.
- vi. New catalysts for transformations during liquefaction.
- vii. Optimization of process conditions.
- viii. Decoupling of thermal and catalytic processes.
- ix. Defined specifications for fuels of the future.

B. Mobil's "Indirect Liquefaction Approaches"

W. Lee discussed Mobil's indirect liquefaction development. This is a proprietary process for the conversion of methanol to high quality gasoline employing Mobil's high-silica, small-pore ZSM-type catalysts. Process conditions are mild (775° F, 25 psig, 1.0 LHSV). The catalytic reaction is highly selective and yields 44% hydrocarbons, 56% water, and only traces of ether, methanol, carbon oxides, and coke. Heat release in the process is substantial, but can be controlled with

light gas recycle for a fixed-bed reactor. Workers at Mobil are currently developing a fluid-bed version in a 4 bbl/day pilot plant and are negotiating with a German company for a semiworks fluid-bed demonstration. The hydrocarbon product is about 60% C_5^+ gasoline, the remainder being light olefins and paraffins. Of the total yield of 9 lb RVP gasoline after alkylation, 88% is produced from the hydrocarbon products. The clear octane numbers are 96.8 F-1 and 87.4 F-2.

Dr. Lee presented data for a conceptual commercial plant. These are listed below.

Feed

Coal, MT/day	27.3
Water, g/min.	6,000

Product

Gasoline, bbl/day	23,065
SNG, MMSCF/day	152.6
Fuel oil equivalent, bbl/day	45,560
Thermal efficiency, %	63

Investment, \$M

Gasification	1,475
Synthesis	<u>205</u>
Total	1,680

Gasoline cost, equity at 12% DCF, ¢/Gal.	93
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According to Lee, the \$0.93 estimate has been obtained on the same basis as \$1.33 per gallon for gasoline by the Sasol (FT) route .

The specified Mobil technology combines proven commercial technology for coal gasification and methanol synthesis very effectively with exciting new catalytic chemistry to produce a premium product. Though still costly relative to gasoline from imported crude oil, it looks like a route that could be commercialized quickly with a high chance of success. Furthermore, improvements in coal-gasification technology over the dry-bottom Lurgi process (their base case) could reduce the major component in the capital cost. It is interesting to note that Mobil has been contacted by the Germans to build a semiworks fluid bed plant and by New Zealand concerning a fixed-bed commercial project. This U.S. invented technology may well be first commercialized outside of the United States.

C. Presentation by W. Lee of Mobil

The Mobil process for the methanol-to-gasoline process is described in Figs. AC-7-1 to AC-7-5.

Fig. AC-7-1 Conversion of alcohols to gasoline.

Fig. AC-7-2 The ZSM-5 structure; reproduced from Nature 272, 437-38 (1978).

Fig. AC-7-3 Reaction paths in methanol conversion.

Fig. AC-7-4 Reaction paths for methanol conversion to hydrocarbons at 371°C.

<u>Feed</u>	<u>Product</u>
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Material Balance: 100 Tons → 44 Tons + 56 Tons

Energy Balance: 100 Btu → 95 Btu + 0 Btu

Fig. AC-7-5 The chemistry of methanol conversion to gasoline.

AC-8.1 REPORT ON DISCUSSIONS WITH STAFF MEMBERS
OF THE EXXON CORPORATION,
PRINCETON, NEW JERSEY (AUGUST 17, 1979)

R. Schlossberg and L. Vernon from Exxon made presentations. These contained a substantial amount of new material.

Schlossberg noted that the primary structure in coal consists of C-C, C-H, and C-O bonds. These bonds may break by either a free radical or ionic mechanism. The secondary structure consists of weaker interactions such as π - π bonds and H-bonds (5 to 15 kcal per mole).

R. Schlossberg then revisited the well known Friedel-Crafts reaction on coal, specifically the reaction of coal with isopropylchloride and aluminum trichloride. By the use of mass spectroscopy, he showed that the product represented chemical attack on the coal, not dissolution of the coal in other reaction products. He also showed that the derivatized coal gave better liquefaction yields in tubing bomb experiments. Areas for future exploration suggested were the following:

- i. What is the Lewis acid catalyst doing to coal?
- ii. How are the alkylated products related to coal?
- iii. Is the mass transport of the system being altered?
- iv. Can a new, practical process be developed from these observations?

L. Vernon reported on coal liquefaction mechanism studies. He chose an appropriate model compound, diphenyl, and studied its hydrogenation at 450° C, both with and without tetralin. Bibenzyl is known to cleave into radicals with an activation energy very close to that involved in coal liquefaction. His analysis

and rate studies show that direct hydrogenation can occur by a free radical mechanism in the absence of a donor solvent. In the presence of tetralin, hydrogenation occurs by H transferred from the solvent, as well as by direct hydrogenation. He presented a mechanism that is consistent with the observed kinetics and product distribution. This mechanism is, however, not unique and some alternatives (suggested by John Ross) involve ionic rather than radical reactions for the step in which tetralin is a catalyst. Vernon's work does rule out the accepted mechanism for donor-solvent action as the whole process.

AC-8.2 REPORT OF A VISIT TO THE
DEPARTMENT OF CHEMICAL ENGINEERING,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(OCTOBER 11, 1979; BY S. S. PENNER)

According to J. B. Howard, the total annual research program on coal-related studies in the Department of Chemical Engineering at M.I.T. is about $\$3 \times 10^6$ per year. This program is supported by DOE, EPA, NIH, NSF, Exxon Corporation, several utility companies, and other sponsors.

A. J. B. Howard and W. A. Peters described the results of extensive studies on pyrolysis, hydrocracking, and hydropyrolysis performed in a specially designed reactor. This reactor has two perforated, electrically-heated plates between which small particles (10 μm to 1 mm) of coal, lignite or cellulose are heated at controlled rates. Temperature-time profiles and gas composition vs. time profiles are mapped. The gas analyses are performed on cooled samples that are withdrawn at defined time intervals. Pressures up to several hundred atmospheres, heating rates of 600 to 12,000°C/sec, and temperatures up to 1300°C have been utilized.

This work is fully described in the appended list of references.

I believe that it would be useful to apply Howard's pyrolysis and hydro-pyrolysis apparatus for routine testing of all of the coal samples that will be collected and studied by Neavel. The work at M.I.T. has thus far been restricted to studies of a Montana lignite and a Pittsburgh seam bituminous coal. The results obtained on pyrolysis rates have been correlated by using a Gaussian distribution of activation energies in a set of first-order decomposition reactions.

References

1. D. B. Anthony, J. B. Howard, H. P. Meissner, and H. C. Hottel, "Apparatus for Determining High Pressure Coal-Hydrogen Reaction Kinetics Under Rapid Heating Conditions," Rev. Sci. Instrum. 45, 992-995 (1974).
2. D. B. Anthony, J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," Fifteenth (International) Combustion Symposium, pp. 1303-1317, The Combustion Institute, Pittsburgh, Pa., 1975.
3. D. B. Anthony, J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization and Hydrogasification of Bituminous Coal," Fuel 55, 121-128 (1976).
4. D. B. Anthony and J. B. Howard, "Coal Devolatilization and Hydrogasification," AIChE Journal 22, 625-656 (1976).
5. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Composition and Kinetics of Lignite Pyrolysis," I and EC Process Design and Development 17, 37-46 (1978).
6. P. C. Lewellen, W. A. Peters and J. B. Howard, "Cellulose Pyrolysis Kinetics and Char Formation Mechanism," Sixteenth (International) Combustion Symposium, pp. 1471-1480, The Combustion Institute, Pittsburgh, Pa., 1977.
7. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Compositions and Formation Kinetics in Rapid Pyrolysis of Pulverized Coal - Implications for Combustion," Seventeenth (International) Combustion Symposium, pp. 117-130, The Combustion Institute, Pittsburgh, Pa., 1979.
8. E. M. Suuberg, W. A. Peters, and J. B. Howard, "A Comparison of the Rapid Pyrolysis of a Lignite and a Bituminous Coal," Symposium on Thermal Hydrocarbon Chemistry, Division of Petroleum Chemistry

and Fuel Chemistry, American Chemical Society, Anaheim, Calif., March 12-17, 1978.

9. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Compositions in Rapid Hydropyrolysis of Coal," submitted for publication to Fuel (1979).

B. C. N. Satterfield has performed studies on model compounds (e. g., thiophene, quinoline, pyridine) of interactions between hydrodesulfurization and hydrodenitrification at pressures to 10^3 psia and temperatures of several hundred °C. These studies have been performed in a continuous flow micro-reactor and suggest that the presence of H_2S may enhance denitrification. Current studies involve the use of nickel-molybdenum catalysts in a trickle-bed, liquid-phase reactor.

References

1. C. N. Satterfield, M. Modell, and J. F. Mayer, "Interactions Between Catalytic Hydrodesulfurization of Thiophene and Hydrodenitrogenation of Pyridine," A.I. ChE Journal 21, 1100-1107 (1975).
2. J. F. Cocchetto and C. N. Satterfield, "Thermodynamic Equilibria of Selected Heterocyclic Nitrogen Compounds with Their Hydrogenated Derivatives," Ind. Eng. Chem. Process Des. Dev. 15, 272-277 (1976).
3. C. N. Satterfield and J. F. Cocchetto, "Pyridine Hydrodenitrogenation: An Equilibrium Limitation on the Formation of Piperidine Intermediates," A.I. Ch. E. Journal 21, 1107-1111 (1975).
4. C. N. Satterfield, "Trickle-Bed Reactors," A.I. Ch. E. Journal 21, 209-228 (1975).
5. C. N. Satterfield, M. Modell, R. A. Hites, and C. J. Declerck, "Intermediate Reactions in the Catalytic Hydrodenitrogenation of Quinoline," I and EC Proc. Des. and Dev. 17, 141-148 (1978).

Satterfield is currently also working on indirect coal liquefaction using slurries in an autoclave and finely divided catalysts. The hope is to develop procedures that produce efficient conversions at greatly reduced $(H_2)/(CO)$ ratios. The apparatus has automated microprocessors with three chromatographs that allow continuous analysis of C_1 to C_{15} compounds, including the oxygen compounds formed by reaction between H_2 and CO. Contact times are seconds to minutes and a variety of catalysts will be used. The autoclave has a capacity of 1 liter but generally holds only about 300 cc.

C. J. P. Longwell has been involved in defining study programs to optimize the refining and application technologies of coal-derived liquids.

Longwell's work has involved primarily the reoptimization of aircraft turbines in a study performed for NASA. He believes that it is especially desirable to develop engines that can accept a wide spectrum of readily available fuels, especially diesel fuel. To facilitate this objective, he would like to see the development of special refineries with capacities of a few hundred barrels per day that are used to process selected fuels for engine testing from coal-derived (e.g., SRC II) and other liquids.

The current constraint of less than 20% aromatic contents on aviation fuels should be raised to 35% aromatics (i.e., the highest levels that are likely to be encountered in shale-oil-derived fuels).

Longwell's stated objective of broadening the fuel cuts usable in aviation engines requires engine development, especially the design of two-stage combustors to reduce peak temperatures and overheating of liners with sooting fuels. At the same time, engines should be developed for specialty fuels (e.g., H_2 or

H₂-derived fuels) and for accepting a very wide range of fuels (e. g., Stirling-cycle steam engines).

NASA is the primary current contractor for studies of reoptimization of combustion systems, although it is apparent that DOE also has an important role to play in this field. These studies should include considerations of fuel thermal stability and the design of burners to control fuel-nitrogen conversion to compounds other than NO_x. Thus, in aircraft engines, one should use a pilot-plant igniter for near-stoichiometric mixtures and add fuel downstream to maintain low temperatures; in boilers, it is desirable to burn fuel-rich mixtures to minimize NO_x production and then to add more air in order to burn particulate formations.

Longwell's goal is fuel-system flexibility for properly designed engines. With flexibility, H₂ requirements can be reduced. A 1% increase in H₂ requirements corresponds roughly to a reduction in aromatics contents from 35 to 25% and a fuel-cost increase of 10%.

D. P. S. Virk is exploring the utilization of the Woodward and Hoffman rules in order to define concerted reactions that will allow more efficient splitting of coal structures at greatly reduced hydrogen consumption.

Reference

1. P. S. Virk, "Pericyclic Pathways for 1,2-Diphenylethane Decomposition," Fuel 58, 149-151 (1979).

AC-8.3 REPORT ON THE EPRI COAL-LIQUEFACTION REVIEW
(MAY 9-10, 1979; PARTICIPANTS: S. A. ALPERT, F. LEDER,
S. S. PENNER, E. REICHL, J. ROSS, R. SIEG, A. SQUIRES,
J. THOMAS, L. TOPPER)

The meeting agenda is appended. Copies of all of the papers presented at the conference are available to FERWG members.

The presentations and papers dealt with empirical studies. Considerable emphasis was placed on the important hydrogen-transfer capabilities of the lighter fraction of recycled Kerr-McGee material.

Detailed evaluations and recommendations by F. Leder and by A. M. Squires are attached.

AGENDA

Wednesday, May 9, 1979 (MAXIMUS SOUTH)

	8:00 a.m.	Registration	
	8:10 - 8:20 a.m.	Rovesti's Welcome and Instructions	
		<u>Session I Chairman: Howard Lebowitz</u>	
Paper No. 1	8:20 - 9:10 a.m.	"Improved Coal Liquefaction Technology"	
		C. J. Kulik and H. E. Lebowitz - EPRI	
Paper No. 2	9:10 - 9:55 a.m.	"Response of Product and Solvent Composition to Catalyst Deactivation During Coal Liquefaction"	
		T. O. Mitchell - Mobil R & D Corporation	
Paper No. 3	9:55 - 10:40 a.m.	"Western Coal Liquefaction"	
		H. F. Silver - University of Wyoming	
	10:40 - 11:00 a.m.	Coffee Break - (Lobby Area)	
	11:00 - 12:00 noon	Discussion - (Mezzanine Area)	
Paper Number:		Discussion Leaders:	Rooms:
1		Art Squires	Patrician I
2		Ricardo Levy	Patrician II
3		Linda Atherton	Patrician III
	12:00 - 1:15 p.m.	LUNCH (Maximus Central)	
		Ron Fischer - DOE Coal Liquids Refining Program	
		<u>Session II Chairman: Jerry Fox</u>	
Paper No. 1	1:15 - 1:55 p.m.	"Critical Solvent Deashing of Residual Coal Derived Liquids"	
		H. E. Lebowitz - EPRI	
Paper No. 2	1:55 - 2:40 p.m.	"Catalytic Upgrading of Regular and Short Contact Time SRC"	
		P.J. Angevine, R.H. Heck, S.S. Shih, T.R. Stein - Mobil	
(no discussion)	2:40 - 3:00 p.m.	"The Effect of Carrier Gases and Solid Heat Carrier on Tar Yield and Quality of ORC Flash Pyrolysis"	
		S. C. Che - Occidental	
Paper No. 3	3:00 - 3:40 p.m.	"Solids Formation During the Liquefaction of Western Coal"	
		R. G. Jenkins - Penn State	
	3:40 - 4:00 p.m.	Coffee Break - (Lobby Area)	
	4:00 - 5:00 p.m.	Discussion (Mezzanine Area)	
Paper Number		Discussion Leaders:	Rooms:
1		Nandor Herskovits	Patrician I
2		Bill Weber	Patrician II
3		Frank Tiller	Patrician III
	6:30 - 7:30 p.m.	No Host Coctails - Maximum Central	
	7:30 p.m.	DINNER - Maximum Central	
		Dwain Spencer - "Legislative Initiatives to Foster Commercialization of Synthetic Fuels"	

Thursday, May 10, 1979 (MAXIMUM SOUTH)

8:00 - 8:10 a.m. Linda Atherton - Remarks

SESSION III Chairman: Linda Atherton

Paper No. 1 8:10 - 8:55 a.m. "Conventional and Short Residence Time Coal Liquefaction Using Selective Product Recycle"
J. A. Kleinpeter and Francis P. Burke, Conoco Coal

Paper No. 2 8:55 - 9:45 a.m. "Catalyst Development for Liquefying Eastern and Western Coal"
K. K. Robinson and D. Kim - Amoco Oil

Paper No. 3 9:45 - 10:35 a.m. "Properties & Liquefaction Behavior of Western Coals in Synthetic Recycle Solvents"
D. D. Whitehurst - Mobil R & D Corp.

10:35 - 10:45 a.m. Remarks: S. B. Alpert

10:45 - 11:05 a.m. Coffee Break (Lobby Area)

11:05 - 12:05 a.m. Discussion (Mezzanine Area)

Paper Number:

Discussion Leaders:

Rooms:

1

Howard Lebowitz

Patrician I

2

Bill Rovesti

Patrician II

3

Howard Silver

Patrician III

12:05 - 1:15 p.m.

LUNCH (MAXIMUM CENTRAL)

Ron Wolk - Concluding Remarks

SESSION IV Chairman: Norman Stewart

Paper No. 1 1:15 - 2:00 p.m. "Effect of Solvent Properties in the SRC Process"
Bill Weber - Catalytic (EPRI), G. Styles - Southern Company Services

Paper No. 2 2:00 - 2:45 p.m. "The Evaluation of Selective H-Coal Catalysts"
A. G. Comolli, E.S. Johanson and D.T. Huibers - HRI

Paper No. 3 2:45 - 3:30 p.m. "Liquefaction of Western Subbituminous Coals with the EDS Process"
K. Trachte - Exxon

3:00 - 3:35 p.m. Remarks - Bill Rovesti

3:35 - 3:55 p.m. Coffee Break - (Lobby Area)

3:55 - 4:55 p.m. Discussion (Mezzanine Area)

Paper Number

Discussion Leaders:

Rooms:

1

Conrad Kulik

Patrician I

2

Heinz Heinemann

Patrician III

3

Ev Gorin

Patrician II

AC-8.3A OVERALL IMPRESSIONS OF THE EPRI CONFERENCE
ON COAL LIQUEFACTION (BY F. LEDER)

- A good deal of the work is concerned with incremental improvements in existing technology.
- Fundamental studies in kinetics were not emphasized. Instead, overall yields and gross conversion rates were estimated.
- Heavy emphasis was placed on hydrotreating in solution as in SRC II and EDS technology. Pyrolysis was mentioned only briefly and Fischer-Tropsch synthesis was not discussed.
- A new development emerged, namely, supercritical extraction and fractionation of coal as developed by workers at the Kerr-McGee Corporation. This discovery is potentially important and may provide a new unit process for inclusion in other liquefaction schemes.
- A great deal of work is being generated on catalysts and on model compounds. Work on bimodal catalysts and bi-metallics provides a good base line for state-of-the-art hydrogenation technology.

Recommendation: EPRI, as well as DOE, should fund more work of a fundamental nature. Basic kinetics, reaction mechanisms and conversion routes need to be elucidated so that major steps forward will occur.

AC-8.3B COMMENTS ON EPRI COAL LIQUEFACTION
CONTRACTORS' CONFERENCE (BY A. M. SQUIRES)

This Note comments upon some aspects of the recent Conference in Palo Alto, bringing in items discussed during the FERWG visit to Ft. Lewis on May 11. The emphasis will be upon (a) leads for fundamental research in coal chemistry and (b) difficulties standing in the way of such research that may require special measures to assist workers who would undertake the studies.

1. Leads for Research - Recycle of Heavy SRC Species

The Kulik-Lebowitz paper that led off the EPRI Conference contains exciting leads for fundamental work in coal chemistry to determine the precise chemical mechanisms that underlie the essentially engineering phenomena reported in the paper. In brief, the Kulik-Lebowitz paper presents a set of liquefaction data for which the simple explanation is that SRC product contains moieties of peculiarly "super" donor solvent power through their virtue as "shuttles" to convert gas-phase hydrogen onto the solubilized coaly matter. Although other, more complex explanations were attempted in the discussion of the paper, it seems most improbable to me that the simple explanation will not hold up. It should perhaps be emphasized that the Kulik-Lebowitz data show that the "super-donor" species are present in the solvent in relatively small amounts.

In the light of the Kulik-Lebowitz paper, it was interesting to learn during the visit to Ft. Lewis that the operators of the SRC pilot plant there had independently come to the belief that the SRC product itself contains moieties from coal whose return to the dissolver caused "good things" to happen. This was viewed as a benefit of the recycle stream in the SRC II Process and is independent of the benefit to be derived by recycle of ash matter and the building up of the concentration of ash matter in the SRC dissolver.

The beauty of the Kulik-Lebowitz disclosures is that the Kerr-McGee Critical Solvent Deashing Process provides a means for selecting those moieties in the

SRC process whose recycle to the reactor will do the most good - or will do the particular "good" that the process design engineer wishes to have accomplished for his particular process. One can visualize a whole range of processes using this new tool for different process objectives.

The Kerr-McGee Process is a new approach to the fractionation of hydrocarbonaceous matter, allowing the separation of fractions of such matter that are heavier than anything that could be distilled. Clearly, chemical engineering researchers must take note of this development, and consider its needs by way of fundamental chemical engineering research to extend its power.

From the point of view of the coal chemist, he now faces an urgent task to discover which particular species are the "ingredient X" that make Kerr-McGee "light SRC" such a good hydrogen shuttle.

The combined effect of such research may be a greater selectivity toward the ingredients whose recycle will do the most "good".

2. Leads for Research - Need for a Test Characterizing Coals for Liquefaction

On March 23, FERWG heard from Exxon about the extreme discrepancy in liquefaction behavior of two Illinois No. 6 coals in the Exxon Donor Solvent Process. The two coals, Monterey and Burning Star, give relatively good and relatively poor performance in the primary coal-dissolution step of the process, respectively, yet the two coals differ relatively little in the "classical" tests for characterizing coals. At the March FERWG meeting, Dr. John Scott urged that an important research objective ought to be the development of a test to characterize a coal for donor-solvent liquefaction. (It might be noted that the relative merit of Monterey and Burning Star coals are reversed in the H-Coal Process, compounding the sense that we need to know much more.)

The EPRI Conference brought out further paradoxes of this type in the form of data presented by Dr. Duayne Whitehurst of Mobil Research & Development Co. on the liquefaction behavior of a series of samples of subbituminous coal (from the Wyodak seam) taken from the same large drum-sample. The sub-set of samples

varied enormously, both in early-time liquefaction conversions and in percentage aromaticity.

The personnel at Ft. Lewis told us of the paradoxical behavior of four lots of Pittsburgh Seam coal that had been processed in the SRC II mode at Ft. Lewis: Blacksville No. 2 and Loveridge Mine gave poor performance, and Powhatan No. 5 and Ireland Mine, good. We were not given coal characterization data on these coals, and it will be important to obtain such data to reinforce the point that FERWG will wish to make concerning research on better tests to predict such behavior.

3. Difficulties for the Researcher Who Would Do Basic Research on Coal

FERWG will need to discuss certain difficulties that stand in the way of the researcher who would undertake basic research to resolve some of the foregoing matters - especially the researcher who works in an institutional setting relatively isolated from the large coal R & D establishments.

One difficulty is illustrated by the amount of information that was coded or kept confidential during the EPRI Contractors' Conference. The reasons for this are clear: EPRI cannot be expected to reveal all of the details of the operation of the Kerr-McGee Process to secure the "light SRC's" used in the Kulik-Lebowitz studies. Kerr-McGee is performing a service to the Nation by developing its Process for use in de-ashing SRC and cannot be expected to disclose all of the details of its process to the general public. Exxon's Solvent Quality Index is proprietary information that Exxon evidently regards to have competitive value.

Given the nature of EPRI as an institution, it seems probable that the full details of its studies of recycled light SRC's will remain secret for only a relatively short time. One cannot be so confident that Kerr-McGee and Exxon will be forthcoming with additional information very soon.

Given the hard fact, however, that confidential information exists, the would-be researcher into the fundamental bases for the phenomena reported upon faces two difficulties: how is he best to plan his work, and will he be "scooped" when he is at the point of publication by revelations that make his own work seem

pointless and a waste of time? (Has the latter risk deterred work on supercritical gas extraction of coals in the United States, simply because everyone knows that the National Coal Board is sitting upon such a mountain of data? It is otherwise puzzling that so little work on supercritical gas extraction of coals is underway here.)

Another difficulty has been emphasized to me by Dr. Duayne Whitehurst - both last March in a 'phone call and again at the EPRI Conference. This is the difficulty of obtaining samples of coal and plant materials from operations during which curiosities have emerged. For example, will it be possible now to obtain from Ft. Lewis or Exxon samples of coals and products made during runs on the specific coals mentioned above?

AC-8.4 CONFERENCE ON UNIVERSITY COAL LIQUEFACTION
CONTRACT RESEARCH (SEPTEMBER 6-7, 1979;
BY JON CLARDY)

This is an annual gathering in which all university groups with DOE funding for coal research meet. This year's format was changed to have one hour presentations by selected speakers rather than 10 minute talks by everyone and to focus on coal liquefaction. There has also been a change to decentralize the management of contracts and some levity was provided by the scramble of university researchers to meet their new managers. Abstracts and research accomplishments of all contracts related to coal liquefaction were given out and I include a copy for reference. My overwhelming impression, which was borne out by every nonspeaker I chatted with, was that very little new material was presented.

1. Ronald H. Fischer

The advanced research and development objectives are to "explore innovative process concepts having a potential for significant cost reduction in synfuels production, to provide a fundamental understanding of the chemistry of coal conversion processes, and to explore new coal chemistry". Fischer is very excited about research in this area and picked two topics on which he felt a great deal remains to be done and in which universities could contribute.

A. Disposable catalysts program for hydroliquefaction.

The motivation for this is to reduce hydrogen consumption substantially and increase liquid product yield. Current technology uses

excessive hydrogen, i.e. much more than would be theoretically required to make a premium fuel and hydrogen production is estimated to be one-third of the capital cost and 35% of the operating cost of planned plants. The idea is to use the mineral matter in coal or some other inexpensive ore as coal liquefaction catalysts. He hastened to add that this was not a new idea and could be traced to Bergius. He then summarized a series of studies at Sandia that showed that a 5% pyrite addition was roughly equivalent to a 20°C reduction in temperature for a number of coals. There was also an effect of surface area - the more the better in terms of liquid yield. Of course the amount of solid added makes this unattractive for practical processes. What needs to be done:

- 1) in situ study of iron sulfides during liquefaction
- 2) study of stoichiometry of pyrrhotites in residues as a function of variables
- 3) determination of the limitations of pyrrhotites as catalysts
- 4) exploratory research involving use of other inexpensive minerals as catalysts.

Pyrrhotite seems to be the approved way to describe nonstoichiometric "FeS".

Mr. Fischer also addressed outstanding research opportunities in indirect liquefaction. The stated objective of this program is "to produce transportation fuels from synthesis gas at high selectivity and efficiency". Three areas could be improved:

- 1) better integration of gasification and fuel forming steps
- 2) limit chain growth by use of shape selective catalysts
- 3) more thermally efficient reactions

A suggested attack on the first problem could be to use a gasifier which produces synthesis gas having a low H_2/CO ratio in conjunction with a liquefaction reactor which uses the Kolbel reaction, i.e. $3CO + H_2O \rightarrow 2CO_2 + CH_4$. The advantage to this is that a separate shift reaction is not required and the overall process produces less H_2O (steam). The two processes are compared in the following scheme.

COMPARISON OF STOICHIOMETRY FOR NORMAL SYNTHESIS AND KOLBEL SYNTHESIS

GASIFICATION	$12 \text{ CH}_{1/2} + 6 \text{ H}_2\text{O} + 3 \text{ O}_2 \rightleftharpoons 9 \text{ H}_2 + 12 \text{ CO}$	
	NORMAL F-T	KOLBEL F-T
SHIFT	$9 \text{ H}_2 + 12 \text{ CO} + 5 \text{ H}_2\text{O} \rightleftharpoons 14 \text{ H}_2 + 7 \text{ CO} + 5 \text{ CO}_2$	NOT REQUIRED
SYNTHESIS	$14 \text{ H}_2 + 7 \text{ CO} \rightleftharpoons 7 \text{ CH}_2 + 7 \text{ H}_2\text{O}$	$9 \text{ H}_2 + 12 \text{ CO} \longrightarrow 7 \text{ CH}_2 + 5 \text{ CO}_2 + 2 \text{ H}_2\text{O}$
OVERALL	$12 \text{ CH}_{1/2} + 11 \text{ H}_2\text{O} + 3 \text{ O}_2 \rightleftharpoons 7 \text{ CH}_2 + 5 \text{ CO}_2 + 7 \text{ H}_2\text{O}$	$12 \text{ CH}_{1/2} + 6 \text{ H}_2\text{O} + 3 \text{ O}_2 \longrightarrow 7 \text{ CH}_2 + 5 \text{ CO}_2 + 2 \text{ H}_2\text{O}$

The shape-selective catalyst story was essentially the ZSM-5 discussion we heard at Mobil. It was felt that this was the only way to get away from the "Schulz-Flory" distribution of products.

The need for more thermally efficient syngas conversion reactors was also discussed but this was not directly relevant to our concerns.

The question period did elicit some more details about the catalytic activity of pyrite. It has no apparent effect on the cleavage of dibenzyl into radicals, the model system that L. Vernon (Exxon) discussed with us, but does catalyze the conversion of tetralin into methylindane. This is a very poorly understood area.

2. N. Deno (Penn State) discussed the application of a newly developed and somewhat bizarre oxidation reaction to coal structure and chemistry. Normal oxidations burn off aliphatic carbons to leave an aromatic acid residue while Deno's reaction ($\text{H}_2\text{O}_2\text{-CF}_3\text{CO}_2\text{H-H}_2\text{SO}_4$) burns away the aromatic part to leave aliphatic acids. [I did not believe the original claims for this reaction and reinvestigated it casually. It is simply remarkable. A crudely crushed coal dumped into this reagent turns into a water-clear solution overnight!] This work is still in the exploratory stages but it appears to be quantitative and should yield some very interesting information. It may be premature to judge but, if one were forced to use Deno's work to select among the competing coal models, Given's structure is the most compatible. The Deno results are somewhat retrograde in current coal structure thinking because they require large condensed aromatic units.

3. J. Katzer (University of Delaware) talked about his work on model compounds in hydroprocessing - especially hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The HDS work showed that both hydrogenation and hydrogenolysis take place with the relative importance varying with choice

of model. The problem of HDN is much more difficult. It appears that complete hydrogenation of the heteroaromatic ring must occur followed by hydrogenolysis of the C-N bond. This latter reaction is not at all selective and substantial C-C cleavage also occurs. The problem is exacerbated by the observation that basic N model compounds such as quinoline are poisons for such hydroprocessing catalysts as Ni-Mo/Al₂O₃. Considerable work on HDN is needed.

4. R. Robinson (Oklahoma State University) described experiments to obtain phase equilibrium data on coal-derived fluids. The most interesting point was that at temperatures up to 400°F and pressures up to 2000 psia the parameters are well described by the Soave-Redlich-Kwong equation with empirical binary interaction parameters for the paraffin-aromatic pairs only.

5. P. Given (Penn State) summarized much of the recent work from that laboratory. The first part of his talk was a detailed excursion into statistics. They had attempted "to establish a base from which conversion, mineral matter effects, product composition, dynamics, etc., in liquefaction can be predicted from such characteristics of the feed-stock as the various parameters related to rank, petrographic composition and mineral distribution." After a lengthy excursion into cluster and factor analysis the situation was far from clear and he stated that "we don't know what all of this means". He suspects that it means that the ideal of a "single band in coal metamorphosis is nonsense". Refreshing candor and possibly a cautionary note for the Exxon program.

He also described some work on the catalytic activity of coal minerals, pyrite and pyrrhotites, in liquefaction. They found pronounced effects at elevated temperatures but minerals from different coals had widely different effects. They are endeavoring to identify the crucial variables.

[As a result of Fischer's talk and this type of work the nomenclature of coal scientists has changed rapidly. There is no longer any "ash" in coal but rather "minerals".]

6. W.H. Wiser (University of Utah) described several aspects of the Utah coal program. He began with his own studies and presented his model of coal. This model was severely criticized in the question period and in my opinion many parts of it do seem to have been whimsically arrived at. He presented model compound studies with N-benzyltetrahydrocarbazole. It was not entirely clear whether this was a first or second order process or whether it occurred in the liquid or gas phase. No further comments are needed.

He also presented some nice ^{13}C NMR work by D.M. Grant. In this study both solid coal and coal-derived liquids obtained by ZnCl_2 treatment were studied. This work was consistent with a liquefaction mechanism that is the reverse of the Friedel-Crafts alkylation.

7. H.C. Dorn (VPI-SU) also spoke about new analytical developments. The use of high temperature ^{13}C NMR appears to be a useful quantitative technique for coal characterization and a convincing story about the use of CF_3COCl as a ^{19}F NMR reagent was given. The fluorine reagent is also useful for characterizing heteroatoms.

These analytical techniques, at present, do not show differences between coals that perform very differently in the SRC process. He reiterated the point that coal performances "may be related to subtle differences in the chemistries of the respective coals."

8. J.A. Guin (Auburn) presented work closely related to Katzer's and Given's on coal mineral catalysis. In his work on benzothiophene he

concluded that pyrite is a good hydrogenation but a poor hydrogenolysis catalyst. He also stressed that phase equilibria are not well known in coal conversion processes and most operating conditions appear to be above the critical point. He showed photomicrographs which suggested that pyrite reacts rapidly with hydrogen to give pyrrhotite and becomes quite porous. He has also done some work with Fe_2O_3 (hematite) but the effect of this is not catalytic. It does improve liquefaction yields but stoichiometric amounts (based on conversion to pyrite) are needed.

He also discussed the role of solvents and suggested NMR criteria for optimum solvent quality. The choice of optimum solvent in SRC processes is coal dependent.

9. C.N. Satterfield (MIT) discussed the advantages of a slurry reactor system in Fischer-Tropsch synthesis. His own reactor is not yet complete. He has reanalyzed literature data to show that the rate becomes mass transfer limited at higher temperatures. This result was not anticipated by earlier workers.
10. N.F. Woolsey (University of North Dakota) talked about the chemistry of preasphaltenes. The major new development appears to be the use of s-triazine as an NMR solvent. The question period reworked the point that the "molecular weights" of a coal and its conversion products are not at all well understood. There does not appear to be any agreement on how to do the gel permeation chromatography experiment. A group at PETC is investigating this and T.F. Yen (University of Southern California) claims to have done it and promises a DOE report will be released soon.
11. A. Davis (Penn State) talked about aging of coal and mineral matter catalysis. The thermoplastic behavior of coal showed dramatic changes

with 20 days exposure to air at room temperature. This was found to have little effect on liquefaction behavior. He also found that the addition of exchangeable cations to 800° chars increased their reactivity in the following order:

Na>K>Ca>Raw>Fe>Mg>Demineralized .

AC-8.5A REPORT OF SITE VISIT TO THE
LAWRENCE BERKELEY LABORATORY

(MAY 8, 1979; VISITORS: S. S. PENNER AND L. TOPPER)

Discussions were held with a number of staff and U.C. Berkeley faculty members at LBL, including A. M. Sessler, C. Judson King, H. Heinemann, G. Somorjai, T. Vermeulen, and K. Westmacott.

The LBL program on fossil-energy research is currently funded at an annual level of about \$600,000 (from BES in DOE) and is expected to grow to about double this level. The work is of high scientific merit and interest and is designed to contribute to fundamental understanding of elementary processes. The Lawrence Berkeley Laboratory is unique among DOE laboratories insofar as extensive involvement of university faculty members and graduate students are concerned: about 150 U.C. Berkeley faculty members and about 450 Ph. D. students are participants in LBL studies.

Fundamental research at LBL includes the following types of studies: catalysis, separations, heat and mass transfer, phase equilibria, chemical rate processes, and combustion studies; also exploratory process research, and instrumentation development. The laboratory personnel view LBL as an under-utilized national resource in the fossil-fuel development area.

The following basic studies relating to coal mining and coal liquefaction are currently in progress: studies of catalysis on single crystals, geological and geochemical impacts of coal mining, processes for the removal of pyritic and organic sulfur prior to coal combustion, homogeneous catalysis under mild conditions, design of process configurations to take proper advantage of catalyst properties, development of novel solvents for extraction, acid-base chemistry as it relates to stripping, coal characterization, studies of pore accessibility, and the relation between chemical reactivities and surface

structures and properties. There are excellent and costly diagnostic facilities [e.g., electron microscopy is now being developed to achieve a spacial resolution of about 5 Å in an "environmental cell" ($\sim 10^3$ °C, 100 atm)].

Model compound studies are in progress to evaluate the role of heteroatoms. Fundamental work on catalysis deals with both Fischer-Tropsch synthesis and with direct liquefaction. Emphasis is on the relation between the microstructure of coal and gasification kinetics.

Hydrocarbon synthesis is being studied on single crystals of rhodium and iron, with particular emphasis on the role of O_2 in effecting conversions. High CO/H_2 ratios have been converted successfully without reactor plugging. Experiments have been designed to identify the possible formation of hot spots during conversion. Controlled deposition of transition metals on coals is being used to study rates of pyrolysis and hydrogenation; the role of organometallics (transition metals) on reactions involving small molecules is being defined. The product selectivity of zeolite catalysts is under investigation. Low-temperature ($\sim 325^\circ\text{C}$) liquefaction in $ZnCl_2$ -alcohol mixtures is being studied.

Workers at LBL estimate the current extent of catalytic research in the U.S. ($\sim \$15 \times 10^6$ per year, including industrial support) to be perhaps one seventh of the level of support that has been shown to be needed for the successful development of catalysts in the petroleum industry ($\sim \$100 \times 10^6$ per year for 20 years).

AC-8.5B REPORT OF SITE VISIT TO THE
LAWRENCE BERKELEY LABORATORY
AND UNIVERSITY OF CALIFORNIA, BERKELEY
(JUNE 18, 1979; BY ARTHUR M. SQUIRES)

Persons seen: Edward Grens
 Judson King
 Heinz Heineman
 Gabor Somorjai
 John Shinn (representing Theodore Vermeulen)
 Russell Blackadar
 William Gillespie
 Philip Ross

I visited Berkeley on June 18 for discussions with coal scientists there on behalf of FERWG. In general, the work underway at Berkeley appears to be of high scientific quality, and much of the work is of "longrange" character, in the sense that it is speculative and not geared to produce results of immediate usefulness to a specific DOE technological program.

Coal "Depolymerization" under Mild Conditions

Vermeulen and Grens in Chemical Engineering at Berkeley have a program involving a number of students in efforts to find new ways to "depolymerize" coal under mild conditions, i.e., at temperatures below the coal pyrolysis range. For example, John Shinn (working for Vermeulen and about to complete his Ph.D. before joining the staff of Chevron Research at Richmond, CA) has obtained high degrees of solubilization of Wyodak subbituminous coal in treatments with ZnCl_2 -methanol mixtures at 275°C under hydrogen at about 14 atmospheres. Methyl groups are incorporated in the pyridine-soluble product (not methoxy groups; the product contains appreciably less oxygen than the starting coal).

The work provides another technique for mild "depolymerization" of coal to prepare material for study by organic chemists interested in the structure of coal.

The work may also constitute a lead for improved coal liquefaction processes in which the primary coal-treating step is conducted under milder processing conditions than hitherto thought possible. The process medium for such processes would appear to require the presence of at least two ingredients:

- (a) a catalyst for rupture of the "scissile" bonds that hold the coal's cross-linked macromolecular structure together; and
- (b) an agent to swell the coal or otherwise improve the penetration of reactants to the interior of the coal's structure.

In John Shinn's work, the two ingredients are ZnCl_2 and methanol, respectively. (As mentioned earlier, methanol participates in the reaction as well as produces coal swelling.)

I regard this work as important. It points up the importance of fundamental research in the following areas:

- (1) Work to identify scissile bonds and obtain measures of their bond strengths.
- (2) Search and development of catalysts for rupturing scissile bonds, especially catalysts that are easier to design for than ZnCl_2 .
- (3) Studies of the interaction of coals with a wide range of liquid media: rates of penetration, degrees of swelling, heats of wetting, etc.

As a (perhaps) minor footnote to the Berkeley work, it may be noted that if methanol is to enter the pool of motor spirits or combustion fuels, the incorporation of methyl groups from methanol into coal liquids, as in Shinn's experiments, may be something to consider.

Waste Water Treatment

Judson King of Chemical Engineering notes that DOE Energy Technology is not giving much consideration today to waste water management. King urges that FERWG recommend to Energy Technology to pay more attention to water recycle and water management, with the view of discharging as little water as possible from coal conversion processes, and this water to have potential pollutants at the highest possible concentration levels. King states that biological treatment will deal with only a part of the chemical oxygen demand (COD) from typical coal-processing waste waters. This means that chemical processing will be needed, and this in turn means integration of such processing with the main conversion process. King believes that not nearly enough attention is being paid today to such considerations.

Pyrolysis and Gasification Studies

Coal pyrolysis is being studied in an "environment cell" incorporated in an electron microscope, to study physical changes that accompany the coal conversion. Also, gasification is being studied in a kind of "underfeed stoker", in which a compacted sample of coal is shoved upward into the gasification zone, with rapid heating and some degree of control of solid residence time as well as gas product residence time. I was not able to observe these experiments, but from their descriptions, they appear to me to be useful.

Catalyst Studies

A large effort is underway to study catalysis on specially prepared metal surfaces of known structure. Alexis T. Bell and Gabor Somorjai are studying the Fischer-Tropsch reaction on such surfaces, and have obtained significant results. They always get a surface monolayer of carbon, but also find there must be some penetration of O-atoms into the metal lattice before it becomes Fischer-Tropsch active. It is not clear whether such O-atoms arise from the support or from CO. It is not clear whether oxygen

in H_2O product comes directly from CO or via an exchange from O-atoms in the support.

Work on hydrocarbon reforming on well-characterized metal surfaces is also in progress.

Albert Levy is looking at the deactivation of Co-Mo catalysts in coal liquefaction (e.g., in the H-Coal Process). He sees a layer of vanadium sulfide and MoS_2 on a spent catalyst from oil hydroprocessing, and a layer of FeS_2 and MoS_2 on a spent catalyst from coal treatment.

Heinz Heineman plans work to try to understand why a H_2/CO ratio of about 0.6 works best in the Fischer-Tropsch reaction in a slurry phase (the Klbel reaction), while a ratio of 2 works best in a fluidized bed.

Heinz Heineman discussed with me the potential role of zeolite catalysts in Fischer-Tropsch synthesis. (I gathered that he plans research in this area, with the object of tailoring the synthesis to give diesel fuel.)

Mobil has a commercial dewaxing process using zeolites in a hydrogen atmosphere, with some four or five commercial installations. The process uses the fact that any straight chain hydrocarbon will go into a zeolite, but immediately rearranges (i.e., aromatizes) and/or cracks, and cannot get out again except as, for example, a C_{12} - species.

Mobil's methanol-to-gasoline work and also use of zeolites in conjunction with Fischer-Tropsch synthesis rest upon this same fact. A striking result is that a physical mixture of an iron Fischer-Tropsch catalyst and a zeolite gave the same result as putting the iron onto the zeolite. This shows that the fragments arising from Fischer-Tropsch synthesis are mobile in the gas phase, can enter the zeolite, and cannot get out again except at permitted sizes.

Heineman told me that Sasol II has a "Mobil part", in which Mobil's dewaxing process is used to convert waxes and oxygenates to fuel oil and gasoline. He said that Sasol III may remove oxygenates from process water over zeolite catalysts.

AC-8.6 REPORT OF A VISIT TO THE
COLLEGE OF EARTH AND MINERAL SCIENCES
PENNSYLVANIA STATE UNIVERSITY
(NOVEMBER 13, 1979; BY J. CLARDY)

The research budget for coal research programs is roughly $\$3 \times 10^6$ /year. In the groups I visited this is mostly DOE money. A breakdown of funding for various programs is given in Appendix I. A group of 30 investigators has submitted a proposal to establish a University Coal Laboratory with DOE funding.

1. P. Given is primarily concerned with coal liquefaction and characterization; Most of my time was spent with him. His most recent effort has been a massive study on the dependence of coal liquefaction on coal characteristics for a sample of 104 coals.

A sample of 104 high volatile bituminous coals from the U.S. was selected and liquefaction behavior in a simple tubing bomb system with tetralin was studied. Liquefaction was judged by pyridine solubility and yields to correlate best with volatile matter content and inversely with vitrinite reflectance. At this point, it became clear that the sample base was not homogeneous and cluster analysis was applied. The coals seem to group naturally into three clusters with S content being the most important variable and rank a secondary variable. For each cluster, the liquefaction yield could be "loaded" onto different coal characteristics.

In practice, this means that large numbers of questions can be answered but not simply. For example, suppose one wanted to know how sulphur content affected liquefaction. The analysis shows:

- a) Group 1 (high rank, medium sulphur) - essentially no effect on conversion yield from organic or inorganic sulphur.
- b) Group 2 (medium rank, high sulphur) - a substantial correlation of conversion with total sulphur.

c) Group 3 (medium to low rank, low sulphur) - a substantial effect on conversion from mineral matter content, no effect from organic sulphur.

This work complements the Neavel effort [Exxon] very nicely.

The other interesting point that came out of my talk with Given was the poor state of coal mineral analysis. A recent round robin of samples gave widely disparate results in various laboratories. Much better analytical methods are needed.

2. W. Spackman and A. Davis are interested in greatly expanding the Penn State Coal Data Base. The logic of this is essentially identical to that we heard for the Neavel program at Exxon. A. Davis would be personally interested in quantitative mineral matter analysis using automated microscopy, FTIR, x-ray diffraction and fluorescence, and SEM. He agrees that this field is not in good shape but expects rapid progress because of current interest in mineral matter catalysis.

Spackman and Given also have a project trying to trace the chemistry of plant materials to coal. They have approached NSF for funding of this study.

3. N. Deno has developed some interesting new oxidation reactions for coal. The work so far has been with model compounds in order to understand the chemistry involved. Serious work on coal is just starting, but very interesting results are anticipated.

AC-8.7 REPORT OF SITE VISIT TO THE
UNIVERSITY OF UTAH
(DECEMBER 4, 1979; BY S. S. PENNER)

Discussions concerning coal-liquefaction technologies were held at the University of Utah with A. G. Oblad, W. H. Wiser, and R. E. Wood. Bench-scale (1/8 to 1/4 inch i.d.) experimental facilities, which have been used to examine the catalytic efficacy of a large number of metal salts in direct coal-liquefaction, were inspected.

A general philosophy on coal liquefaction was described some years ago by Oblad,¹ while essential performance details are given for more than 60 hydrogenation-liquefaction processes in another publication.²

The principal point made by Oblad et al relates to a problem that was previously discussed at length by FERWG members in connection with the site visit to Conoco. In brief, one should be able to find a catalyst which, in small concentrations and in well defined pressure and temperature ranges, will facilitate the efficient hydrogenation of coals by rupturing only those bonds that need to be ruptured to produce high liquid-to-gas ratios. Interesting work has been done at Utah to define both the catalyst and the desired operating conditions. While the Conoco work involved a ZnCl_2 ("catalyst")-to-coal mass ratio of about unity, the Utah work has been done with metal-to-coal mass ratios of about 0.03. Finely ground coals (40 mesh +) were exposed to concentrated salt solutions and were then dried before entering the preheater and the reactor under hydrogen pressure. Flow in the helical coil reactor ($\sim 1,800$ psia, $475\text{-}525^\circ\text{C}$) tube is expected to be highly turbulent. Conversions up to 70% + were achieved at liquid to gas ratios as high as 8. The most effective catalysts found^{3,4} were ZnBr_2 , ZnI_2 and ZnCl_2 in some tests while ZnCl_2 was found to be best in others.

Work on direct coal liquefaction using small amounts of metal salts as catalysts is currently funded by DOE at the Cities Service Corporation. University-based studies in this field were previously recommended by FERWG after the site visit to CONOCO. The ideas proposed by Oblad, Wiser and Wood appear to be well founded on extensive experience and include notions about pretreating coals to increase porosities (to $\sim 400 \text{ m}^2/\text{g}$), studying bond ruptures that are promoted by selected metal salts present in low concentrations, using moderate processing conditions, identifying the nature of the fluid-flow processes that actually occur in the reactors, etc.

The ultimate challenge, for selected types of coals, remains direct hydropyrolysis under the proper conditions. In this hydropyrolysis, the mineral matter that is normally present in coals will serve the required catalytic functions to effect proper and efficient bond ruptures.

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AC-8.8 REPORT OF SITE VISIT TO THE
SOLVENT REFINED COAL PLANT OF THE
PITTSBURGH & MIDWAY COAL MINING COMPANY
(DECEMBER 20, 1979; BY A. BEERBOWER)

The writer visited the Solvent Refined Coal Plant of The Pittsburgh & Midway Coal Mining Co. on December 20, 1979, to interview Mr. D. R. Canfield, Engineering Supervisor. The purpose was to investigate the nature and extent of the erosion problems in the SRC-II pilot unit.

OBSERVATIONS

1. LET-DOWN VALVE EROSION is typical of that caused by abrasion from fluid-borne particles. The sketch in Fig. AC-8.8-1 shows the pintle rod and tip. The pintle itself is not greatly damaged. Erosion centers on the 0.25 in. lead tip, which is deeply fluted. Since the sealing takes place upstream on the conical surface of the pintle, loss of control is very gradual. Canfield feels that the problem will be less severe on larger units because of the use of wider openings and more reserve metal. The pintle and tip are made from cobalt-cemented tungsten carbide. It has been found that the erosion decreases with lower cobalt content.

2. FEED PREPARATION AND MIXING problems are limited and are largely related to the fineness of grinding in the ball mill. The mill feed is pre-ground to under one inch and the product as used is normally such that 80% will pass through 200 and 100% through 100 mesh.

Fig. AC-8.8-1 Valve rod with pintle; the rod diameter, pintle and tip are drawn to scale.

This fineness gives minimal erosion in the system, but there are penalties which can be overcome by coarser grinding. The problem is basically one of economic balance. Fine grinding requires a good deal more energy, largely in reducing the size of rock particles; slow milling leads to a thick slurry and no settling. Coarser grinding causes more erosion and settling, but does permit faster grinding, better heat transfer in the preheater, and better life of the balls in the mill. Canfield did not feel that research was required on feed preparation. In this context, "coarse" means 100% through 60 or 80 mesh.

3. LINE PLUGGING is an occasional problem, but is not really chronic. Canfield felt that it was probably associated with the use of electric heaters. It is well known that such heaters lead to growth of deposits from hot spots since temperature excursions may occur which result in coking at the sides of the spot. Canfield showed a radiograph of a pipe that was just about solid; it was nominal 4 in. (4.5 OD, 0.67 wall, 3.16 in. ID). The usual method of detection involves measurements of pressure drops, but these generally occur too late for the effective use of preventive measures. Ultrasonic methods have been used to detect coke build-up, with limited success. There is a hot oil system in the unit but this is apparently not hot enough to be useful.

4. PUMP EROSION is not a serious problem since the plunger pumps that are currently in use minimize erosion. Research

on centrifugal pumps (cf. Rockwell International, EPRI AF-853, Project 775-1, Final Report, September 1978) is judged to be adequate. If pumps fail, multiple plunger pumps will surely be usable for scale-up.

5. FRACTIONATOR CORROSION is the most serious problem at the SRC-II unit. This difficulty has been investigated with little success. Progressively more expensive alloys have been used. The erosion rates, based on coupons hung in a tower, are:

low carbon steel, 1.0 in./year; 316 stainless
steel, 0.2 in./year; Hastelloy G, 0.02 in./year
Hastelloy C, negligible.

Since the tower is two feet in diameter and about 60 feet high, alloy cost is a big factor. Certain zones appear to be hardest hit. Electron probe analysis showed nickel sulfide, but no chlorine. In many cases, there were no deposits to analyze since only bright metal remained. The tower has been steamed out when it is down, but this process did not affect the corrosion.

6. FLOW PATTERNS in the reactor were not important for the work, since there was no experience with bogging or other malfunctions of this type. There has been some use of tracers, but not for flow-pattern studies.

IMMEDIATE SUGGESTIONS

I offered the suggestions detailed below.

1. LINE PLUGGING could be detected by a gamma-ray probe such as the AccuRay from Industrial Nucleonics. The hot oil systems can be operated up to 700^oF if they are properly equipped with seal pots, which prevent air from sucking back; the trapped air is soon reduced to nitrogen.

2. TOWER CORROSION may be due to trace amounts of chloride that are too low for the electron probe to detect. Chlorine can be volatilized from NaCl by two processes. Oxidation of sulfur compounds to sulfonic acids, which are non-volatile, can release HCl. Enough air could be leaking in through pump-shaft seals, etc. to provide the necessary oxidant if the sulfur is in a suitable combination. In that case, substantial injection of NaOH into the feed should help. On the other hand, a reducing situation in the tower could release NH₃ which would carry off chlorine as volatile NH₄Cl. Chloride tends to stay close to the metal and act as a "catalyst" or carrier, dissolving metal and releasing it to the oxidant such as sulfur. If this is the problem, steaming would not be sufficient. The tower should be chemically cleaned (e.g., by Dowell, Inc.) after the source of chloride has been removed.

3. FLOW PATTERNS should be measured by using radio-tracer techniques [J. M. Ausman, A. Beerbower and R. E. Olsen, Chemical Eng. Progress Symposium Series, Part VIII, No. 28, Vol. 56, pp 72-75 (1960)].

RESEARCH RECOMMENDATIONS

It is evident that the pintle-valve design makes it vulnerable to erosion by liquid-borne particles. Redesign to eliminate sharp changes of direction should improve the life of the pintle tip greatly. The use of WC that does not employ a cobalt binder is also a possibility.

Pretreatment of the coal by using the Charmbury "benefication" process to remove most of the shale and pyrites by floatation would solve a whole set of problems, possibly all of those attributed to erosion and perhaps even part of the tower corrosion.

A new investigation of the tower corrosion problem would be rewarding. Since the trip, I learned from Jim Keiser at Oak Ridge that Wilsonville is experiencing similar difficulties since changing to the same feed as that used at Dupont, WA (Fort Lewis). Investigation of carbonyl sulfide (COS) formation from air, coal and sulfur is specifically suggested. This is a very active gas (b.p. $\sim 0^{\circ}\text{F}$) and is not detected by the usual gas analysis. It can cause heavy corrosion leading to powdery FeS or Fe_2OS , which would be suspended colloiddally in the bottoms.

AC-9.1 SITE VISIT TO ROCKWELL INTERNATIONAL,
ENVIRONMENTAL AND ENERGY SYSTEMS DIVISION,
FLASH HYDROPYROLYSIS PROJECT
(FEBRUARY 25, 1980)

The following FERWG members visited Rockwell International on February 25, 1980: J. Clardy, S. S. Penner, and R. P. Sieg. Discussions were held with C. L. Oberg, A. Y. Falk, C. A. Trilling, and D. R. Kahn of Rockwell.

A. Process Description

A schematic diagram of the Rockwell coal-hydrogenation reactor is shown in Fig. AC-9.1-1. This system involves adaptation of rocket technology to coal pyrolysis for the production of liquids. Injection occurs through many impinging jet orifices (with impingement angles of approximately 30° between a central stream of comminuted coal and high-temperature hydrogen gas). The developed system is expected to show the following characteristics of rocket reactors: very high mass-flow rates through relatively small reactors, unit sizes that are readily scaled by replication of injector elements and reactor diameters, successful pyrolysis of a very wide variety of coals ranging from bituminous coals to peat.

B. Process Characteristics

The coal-pyrolysis reactions leading to liquid products are nearly thermoneutral. Residence times used in the reactor typically fall in the range 50×10^{-3} to 5 sec. A variety of coals has been tested successfully. The coal is not pretreated. Seventy to ninety percent of the coal passes a 200 mesh screen. A separate catalyst is not used. A 1 ton/hour reactor has an inside diameter of 3 inches and a length of 5 feet; for this throughout, 8 impinging injector sets

ROCKWELL COAL HYDROGENATION REACTOR

REACTOR CONCEPT

SHORT RESIDENCE TIME SYSTEM WITH RAPID MIXING AND REACTION FOLLOWED BY RAPID QUENCH

FEATURES

- ALL FOSSIL FUELS
- NO CATALYST
- SMALL AND COMPACT
- BETTER OPERABILITY AND MAINTAINABILITY
- DENSE PHASE INJECTION OF COAL
- HEAT SUPPLIED BY H₂ PREHEAT
- DRY, FREE-FLOWING CHAR
- VAPOR-PHASE PRODUCT RECOVERY
- LIQUEFACTION OR HIGH Btu GASIFICATION

REACTOR:
500 TO 1500 psia
1200 TO 1900°F
25000 Msec

COAL

HIGH TEMPERATURE HYDROGEN

RECUPERATOR/QUENCH

LIQUID GASEOUS PRODUCTS

Rockwell International
Energy Systems Corp.

CHAR HYDROGEN

79-MA9-24-8CNA

Fig. AC-9.1-1 Description of the Rockwell coal-hydrogenation process for coal liquefaction through pyrolysis.

are used. The longest test duration has been about 3 hours. No indications of significant erosion problems were observed. Temperature measurements have been made near the reactor wall with thermocouples.

With the presently used system, it is difficult to differentiate between mixing phenomena and hydrogenation. The bulk density of the product particles is about one half of that of the inlet coal. Substantially equivalent results have been obtained with the following carrier gases for the coal: N_2 , H_2 , He, CO_2 . Adequate preheating of H_2 is assured by using both electrical heating and partial combustion with O_2 . Test durations have been limited by problems encountered on separating liquids from char in a spherical chamber; it is hoped that this problem will be alleviated by replacing the spherical char-settling chamber by an appropriately designed conical chamber.

C. Contract History

The original DOE contract extended for a period of 55 months (August 1975 to February 1980) and was funded at a level of \$4,550,944. An extension contract is expected to allow program continuation around the end of March 1980. In the meantime, the facility has been shut down since the beginning of February and the operating crew members have been assigned to other tasks.

D. Results and Future Studies

A reliable method of coal feeding has been demonstrated; the coal flow rate is directly dependent on the overall pressure drop. High mixing efficiencies between gas and coal are important and have been achieved by using appropriate kinetic energy ratios at injection (≈ 6). The liquid yield reaches a maximum value of about 37% near a reactor temperature of $1500^\circ F$ while total carbon conversion increases to over 62% at $2000^\circ F$. The Rockwell coal-pyrolysis data generally agree with results derived from smaller scale laboratory tests. While total carbon conversion to gas and liquid is not sensitive

to reactor residence time, the liquid yields decrease quite rapidly with increasing reactor residence times. The effects of reactor pressure on conversion have been found to be small. The liquid-product yields include about 45% of toluene, benzene and naphthalene. The product gas is largely methane (70 to 90%) with very small amounts of CO_2 ($\sim 3\%$) and the balance made up by CO. The percentage by weight of H_2 consumed relative to the weight of coal pyrolyzed lies between 1 and 7%, depending on reactor residence time and temperature (both of which lead to increasing hydrogen consumption as they are raised).

AC-9.2 COAL PYROLYSIS AT THE OCCIDENTAL RESEARCH CORPORATION*

The following discussion is based on the Occidental Research Corporation (ORC) "Flash Pyrolysis" Process, which has been under development at ORC since 1969 and has been tested at the 3 tpd scale.

A. Process Description

The process will be described with reference to a conceptual commercial design. Figure 9.2-1 shows a block diagram of the overall process while Fig. 9.2-2 emphasizes details of the pyrolysis section.

The commercial design involves processing of 22,444 tpsd of coals with 10% moisture and 8.5% ash (W. Kentucky #9 seam bituminous coal). The char produced amounts to 10,317 tpsd at 11,900 BTU/lb and is sufficient to fuel a 1000 MW power station adjacent to the pyrolysis plant. Based on a raw liquid yield of 35% (MAF basis), the yield of hydrorefined oil products is 31,200 bpsd (i.e., approximately 1.7 bbl/ton of MAF coal).

Washed coal is received at the plant by unit train and is stacked in open storage piles. Coal is reclaimed from storage and fed to the coal preparation plant where it is crushed, ground and classified to -60 mesh particles, and dried.

Pulverized coal is transferred to the flash-pyrolysis reactor, where it is contacted with a circulating stream of 1400°F char at 5 times the coal-feed rate. The coal is heated to about 1075°F in a fraction of a second and produces oil, gas and char. The oil and gas products are separated from the char and quenched in 1.5 seconds. A portion of the char product (~ 7 wt. % of the feed coal) is burned in a transfer line burner to reheat the circulating char stream which supplies heat for pyrolysis. The net char product is cooled and sent to

*This report has been prepared by FERWG member F. Leder and critically reviewed by the following FERWG members: J. Clardy, S. S. Penner, and J. Ross.

Fig. 9.2-1 Schematic diagram of the ORC flash-pyrolysis process.

Fig. 9.2-2 A schematic diagram of the flash-pyrolysis section.

storage. Energy is recovered from the flue-gas before it is desulfurized and released to the atmosphere.

Hot vapors from the pyrolysis section are quenched and cooled to recover oil and gas fractions. Oil is fed to the hydrotreater, where low-sulfur fuel oil is produced. Dry gas is compressed and is partly used (after removal of sulfur compounds) as feedstock for hydrogen production by steam reforming and partly as plant fuel.

Hydrotreating of the raw oil in an ebullating bed reactor yields 7745 bpsd of -250°F , 49° API, 0.07% naphtha and 23,464 bpsd of $+250^{\circ}\text{F}$, 4.6° API, 0.5% S fuel oil. The hydrogen consumption is 1700 SCF/bbl. The high boiling fraction of the oil product from the hydrotreater contains char fines that are entrained in the pyrolysis section. The oil is recycled to the pyrolysis reactors, where it is converted to char and lighter oil products.

Elemental sulfur, anhydrous ammonia, and phenols are recovered by conventional acid-gas removal and water treatment.

B. Performance Data

A 3 tpd PDU was operated under ERDA contract to test the process (1975-78). The liquid-yield and quality for two coals are summarized in Table 9.2-1.

The yields of 35% MAF from the bituminous coal and 22% MAF from subbituminous coal correspond to more than twice the Fischer assay oil contents of these coals without hydrogenation.

The liquid yield decreases with increasing residence time, as is shown in Fig. 9.2-3. The reported peak yields occurred at a residence time of 1.5 seconds, which corresponds to the commercial design point. The curves of Fig. 9.2-3 may be fitted by a first order devolatilization/cracking reaction model (see below).

Table 9.2-1 Liquid yields obtained by workers at Occidental Petroleum in flash pyrolysis; data characterization.

<u>Coal</u>		
Rank	Bituminous C	Subbituminous C
Source	W. Kentucky No. 9	Big Horn, Wyoming
<u>Yield</u>		
Wt. %	35	22
Bbl/ton	1.7	1.1
<u>Analysis</u>		
Ultimate, wt. %		
C	80.3	77.6
H	7.0	7.2
N	1.4	1.2
S	2.1	0.4
O	9.2	13.6
Atomic H/C	1.05	1.12
Gravity, °API	-12.6	-9.8

Fig. 9.2-3 Flash-pyrolysis liquid-yield data as functions of residence time.

The char tended to crack which reduced the yield. The use of char-to-coal ratios, in combination with inert transport gas, led to yields as low as 5%. Reactive gases (e.g., steam and CO_2) have been shown to be effective in terminating undesirable reactions that result in low yields.

The raw liquids are heavy and hydrogen-deficient. More detailed characterization is needed. The available results suggest that higher liquid yields do not necessarily lead to substantially heavier liquids.

Limited work has shown that the liquids may be hydrogenated catalytically. A 28° API syncrude was produced by using fixed-bed hydrotreatment on the liquids derived from subbituminous coal over a commercial Co-Mo catalyst; the H_2 uptake was 3100 SCF/bbl. Nitrogen removal of 80% and sulfur removal of 96% were obtained, as well as 98% conversion of asphaltenes and asphaltols to oil. The need for more work, particularly with bituminous-coal-derived liquids, is apparent.

C. Comments on the Pyrolysis Process

Pyrolysis is analogous to fluid, catalytic cracking. It is a simple procedure using proven technology. Application of the product char as a heat carrier is a distinctive feature of the ORC process. This method of heat supply leads to high through-put, is easily scaled up, avoids dilution of product gas with combustion products, and eliminates the need for an oxygen plant. The use of low-pressure service simplifies the design and feeding of solids. Application of the ORC technology to coal and solid-waste pyrolysis in the PDU was generally straightforward. However, the handling of bituminous coal required a special reactor design. The pneumatic transport of char represents a significant departure from the technology used in petroleum fluid coking and cracking to achieve fluidization.

Efficient cyclones are needed to minimize the loss of char fines to the oil-collection system. The cyclone volume accounts for about half of the vapor-phase residence time. A short residence time, higher efficiency gas-solid separations procedure would be a significant process improvement.

Reliable means must be found to perform rapid pyrolysis of caking bituminous coals because these coals produce the highest liquid yields on pyrolysis. Nearly all bituminous coals are moderately or highly caking and tend to plug pyrolysis reactors. Preoxidation or slow stagewise heating to reduce the caking tendency ameliorate this problem but leads to low liquid yields, as was noted earlier.

An entrained flow reactor was designed to handle caking coals without pretreatment and was tested in the PDU with some success. Continuous runs, with durations of up to 22 hours, were achieved with optimal yields. However, the reactor was subject to sudden irreversible fouling and forced shutdown as a result of erratic char flow. Smooth pneumatic transport of char to the reactor is of crucial importance. Since fluctuations and upsets can be expected in practice, additional engineering development will be necessary to achieve a commercially reliable design.

The char yield from rapid pyrolysis of bituminous coal is approximately 50%. Both the heating value and the sulfur content of rapid pyrolysis char are about the same as of the parent coal. Char utilization as a solid fuel therefore requires desulfurization or SO_2 control, as for the parent coal. At ORC, both char desulfurization and combustion have been studied.

AC-10. COSTING OF COAL LIQUIDS

A working group was convened at the UCSD Energy Center (on January 24 and 25, 1980) for discussions on the costing of coal liquids, to compare methodological aspects in costing, and to identify key R&D programs that might lead to reductions in product costs. F. Leder (part time) and R. P. Sieg of FERWG served as co-chairmen of the discussions and S. S. Penner participated on a part time basis. Participants included J. S. Morrison (Exxon Research and Engineering Company, P.O. Box 101, Florham Park, N.J. 07932), R. Nene (Gulf Research & Development Co.; P.O. Box 2038, Pittsburgh, Pa. 15230), B. K. Schmid (Gulf Mineral Resources Co., 1720 So. Bellaire, Denver, Co. 80222), N. G. Moll and G. A. Stuart (Dow Chemical Co., Midland, Mi. 48640), R. T. Struck and W. E. Clark (Conoco Development Co., Research Division, Library, Pa. 15129), and R. N. Quade and J. F. Watson (General Atomic Co., P.O. Box 81608, San Diego, Ca. 92112). W. Häfele (International Institute for Applied Systems Analysis, Laxenburg, Austria) also participated on a part-time basis.

Carefully prepared presentations were presented on the EDS, SRC-II, Dow, and ZnCl_2 processes for coal liquefaction.

Important cost areas include costs for off-site utilities, hydrogen production (about 15% of total costs in the EDS and SRC-II processes and perhaps 28% in the Dow process), and costs for bottoms processing. The use of off-peak power to produce hydrogen may be a desirable procedure. Generally, hydrogen production by electrolysis will be competitive with operations of a balanced plant only if capital costs for electricity generation are less than about \$300/kw_e.

Häfele discussed an interesting proposal to use independently generated H_2 (e.g., from solar or breeder-reactor power stations) as an "integrator" over the long term. This type of procedure is clearly desirable when hydrogen costs are low and will have the potentially important beneficial effect of reducing atmospheric CO_2 input. There was general agreement with Häfele that a systems integration program dealing with the efficacy of off-site hydrogen use should be implemented.

Research recommendations derived from the discussions by the working group on the costing of coal liquids are summarized in Chapter IV of the main text.

APPENDIX D:

COMMENTS BY REVIEWERS

A preliminary version of this report was sent to outside reviewers. In most instances, the comments and corrections suggested by the reviewers were incorporated within the final document. In those cases in which the reviewers' comments could not be easily accommodated, letters for direct inclusion in this report were requested. These are reproduced here without change.

We are especially indebted to the following reviewers for calling needed corrections to our attention: W. R. Grimes (Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830), P. H. Kydd (Vice President/Technology, Hydrocarbon Research, Inc., P.O. Box 6047, Lawrenceville, New Jersey 08648), M. Orchin (Professor of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221), D. K. Schmalzer (Manager, Technology Development, The Pittsburg & Midway Coal Mining Co., P.O. Box 3396, Englewood, Colorado 80155), and R. H. Wolk (Project Manager, Clean Liquid and Solid Fuels, Electric Power Research Institute, 3412 Hillview Avenue, P.O. Box 10412, Palo Alto, California 94303).

OAK RIDGE NATIONAL LABORATORY

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UNION CARBIDE CORPORATION

NUCLEAR DIVISION

POST OFFICE BOX X

OAK RIDGE, TENNESSEE 37830

March 13, 1980

Prof. S. S. Penner
Department of of Applied Mechanics and
Engineering Sciences
University of California, San Diego
La Jolla, California 92093

Dear Professor Penner:

I am sorry to tell you that I have not had the time to give your assessment (FERWG-11, March 1980) the attention that it deserves. I agree that most, and probably all, of the many needs you identify are real and pressing. I have, accordingly, only a few comments to make.

I would probably have put more emphasis than you seem to upon porosity, internal surface and pore size distribution in coals and the changes in these properties upon heating, chemical treatments, etc.

I am not certain that I see a pressing need for further study of "equilibrium solubilities of coal in various (conventional) solvents" (p. 21). I do feel that the U.S. needs considerable study of coal extraction by super critical solvents (and this could perhaps include "equilibrium solubility" though at such temperatures some thermal effects obtain and I am not sure what "equilibrium" is).

I should like to have seen more attention given to indirect liquefaction processes since these may offer the best possibilities for relatively near-term conversion of coals to clean liquid fuels. You do include discussion of them on pages 4 through 8, but, though you have noted several pertinent points, you seem to have missed an opportunity to provide some (to me) important specific advice. As you note, coal gasification is expensive (in an energy sense); second generation gasifiers - such as the Lurgi Slagger or the Texaco - will operate, for improved energy efficiency, with minimal steam and oxygen feeds, and their output gas will have $H_2:CO$ ratios in the range 0.6 to 0.7. Such ratios are far below those needed to avoid catalyst degradation via carbon formation in commercial Fischer-Tropsch or methanol synthesis. One can, of course, use the water-gas shift reaction to obtain the necessary $H_2:CO$ ratio, but there is an energy penalty in

March 13, 1980

this. The ability to use low $H_2:CO$ ratios directly in Fischer-Tropsch or other synthesis is very desirable. It is this desirability that leads to interest in the slurry-phase Klbel reactor which may markedly assist with this problem. The Klbel-Englehardt synthesis, which under carefully controlled conditions can use $CO:H_2O$ mixtures, represents the extreme in this regard and would also seem to be worthy of some study. Along these same lines, I feel that additional study of gas cleanup at high temperatures and pressures might also be a rewarding venture.

Thank you for the opportunity to review the output of your study, which I consider to have been well and carefully done. I regret that I have not been able to be of real assistance to you.

Very truly yours,

W. R. Grimes /nyw

W. R. Grimes

WRG:nyw

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DEPARTMENT OF CHEMISTRY

March 18, 1980

Dr. S. S. Penner,
Professor of Engineering Physics
University of California, San Diego
La Jolla, California 92093

Dear Dr. Penner:

I have gone through your "Assessment of Long-Term Research Needs for Coal-Liquefaction Technologies" rather rapidly and find it an outstanding and comprehensive document with much valuable summary material.

In addition to a number of errors, which have been corrected in the final document, I wish to offer the following comments concerning the discussion on p. AC-185.

The work of Deno could be made much more valuable if it were complemented by the results of oxidations with reagents that oxidize side chains and not rings, e.g. KMnO_4 and HNO_3 . Taken together, these two oxidation techniques would be more revealing than either alone. I am not as sanguine as most people seem to be about the ultimate power of Deno's technique. I am sure ambiguities will arise because alternate structures can give the same product. Furthermore, the knowledge that alkaline KMnO_4 oxidation provided about the aromatic nuclei and the degree of substitution of rings (H. C. Howard, work in the 1940's) was very powerful but fell far short of elucidating the constitution of the clusters in coal.

I certainly enjoyed reading through your report and want to both congratulate you and thank you for sending me a copy of it.

Sincerely yours,

Milton Orchin
Professor of Chemistry

MO/jcc

March 26, 1980

Dr. S. S. Penner
Mail Code B-010
University of California San Diego
LaJolla, CA 92093

Dear Dr. Penner:

I appreciate the effort that the FERWG-II group is making in contacting outside reviewers to insure that the final report on Assessment of Long Term Research Needs for Coal Liquefaction Technologies is both comprehensive and correct. Your prompt attention to correcting several items that I noted during our recent telephone conversation is an example of this attitude.

There are several research areas, in addition to those covered in the report, that I feel need further consideration. These include:

- o Product utilization test programs
- o Residue gasification
- o Analytical workup procedures for raw liquefaction products
- o Prior basic research work funded by OCR, ERDA and DOE
- o Iron phenolate identification and impacts
- o Centrifuge development

Product Utilization Test Programs

The proper economic optimization of a given process always involves the values that are assumed for the products resulting from that process. Test programs are required to establish values for various coal liquefaction products in relation to alternative materials. Coal liquefaction products are inherently lower in hydrogen content than comparable materials derived from petroleum. Product hydrotreating can be utilized to increase the hydrogen content to any desired level. However, it is not clear yet that the hydrogen content standards established for petroleum based fuels are necessary for coal derived liquids. Performance tests on large scale equipment are required to establish the compositional requirements for coal liquids.

Since coal liquefaction products can contain rather large percentages of nitrogen, up to about 2.0 wt%, their combustion with normal techniques can generate NO_x emissions which are above the stringent levels now being promulgated. Improved combustion techniques of the type that utilize staging can reduce NO_x emissions considerably. However, the risk in taking this approach is the potential generation of smoke because of the relatively low hydrogen content of the fuels.

AD-5

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Basic research is required on staged combustion of high nitrogen/low hydrogen fuels to establish reaction mechanisms on a quantitative level. This will enable predictive models to be developed which will determine proper combustion conditions which simultaneously minimize smoke and NO_x formation. If confirmed in large scale tests, the cost of this approach can then be measured against the alternative concept of severe product hydrotreating to establish the same goals.

Residue Gasification

Hydrogen and/or fuel gas generation from liquefaction residues requires a large part, perhaps 30%, of the total investment in a coal liquefaction plant. In view of this massive financial requirement, research should be carried out either to improve reliability or reduce investment. The most significant area requiring further research is the rate of degradation of residues as a function of time, temperature, amount of diluent, and amount of solids. Each of these items is determined by and can be controlled independently by the liquefaction process. Therefore, some tradeoffs could be calculated if a good data base existed on the behavior of liquefaction residues as a function of composition at elevated temperature.

Other areas requiring better definition are refractory life as a function of gasification zone operating temperature and coal ash composition and temperature measurement in the gasification zone at levels of 2200-3000°F.

Analytical Workup Procedures

The analysis of coal liquefaction products depends to a significant degree to how the product is handled prior to reaching the analyst, whether certain materials are removed by distillation prior to being subjected to solvent extraction, and finally to the solvents that are used and the sequence in which those extractions are carried out. Almost every individual laboratory working in this country has developed its own procedure for analyzing products. In some cases specific procedures may be significant to the development of a given process concept and therefore these procedures can be justified.

Sample exchanges between laboratories often do not yield comparable results. This situation makes it extremely difficult to utilize literature information on product yields for comparison purposes. Therefore, a reasonable effort should be devoted to developing standard procedures for handling and analyzing coal liquefaction products.

Basic Research

A large number of projects devoted to collecting basic data have been funded over the years by OCR, ERDA and DOE. A compendium of this work would be extremely valuable in setting priorities for new projects.

Iron Phenolates

The role of iron phenolates in coal liquefaction is not well understood at this time. It is certainly worthy of a definitive program on the chemistry of formation, analytical identification procedures, and reactivity with structural steels, vessel linings, and catalytic surfaces.

Catalyst deactivation due to iron deposition in catalyst pores or on external surfaces may involve phenolate intermediates. Corrosion of distillation towers handling streams boiling in the 350-600°F range may also involve compounds of this type.

Centrifuges

A significant amount of mechanical development work was carried out on centrifuges at the Wilsonville SRC plant. This work led to the successful utilization of a titanium bellows seal in a solid bowl centrifuge that allowed operation at temperatures and pressures of interest. It should be pointed out that in all cases the centrifuges that have been used for the separation of solids from coal liquefaction products have not been designed for the severe temperature levels that are required.

There may be applications involving the separation of solids from low viscosity products for which centrifuges may prove to be the best choice.

I hope that these comments prove useful in identifying additional areas for future research.

Very truly yours,

Ronald H. Wolk
Project Manager
Clean Liquid and Solid Fuels

RHW:sg