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

FOSSIL ENERGY RESEARCH WORKING GROUP (FERWG)

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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 longterm 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.

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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 universitybased scientists and engineers who perform research related to coalliquefaction 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:

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EXECUTIVE SUMMARY

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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 coalliquefaction 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 hew 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 10^{6} /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 coalliquefaction 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).

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• 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). ñ,

 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 H₂ 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 H₂ 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 largescale 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 H₂ 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 , NH₃) 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.

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

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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 ($\overline{(10)}$) and ash ($(\overline{(11)})$) 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 H_2 to form CH_4 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 H_2 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





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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 H₂ 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

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additive to gasoline) or for conversion to high-octane gasoline or to jetand 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 H₂: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.

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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 ZnCl₂-"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 sitevisit 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

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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-lique- faction 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-lique- faction plant (ECLP)	250	projected: 1980-82
	Commercial-scale demonstration plant	~ 25, 000	after 1988
H-Coal (Hydrocarbon Research.	Process development unit (PDU)	3.5	1964-79
Inc.)	Pilot plant	200-600	projected for 1980-82
	Commercial-scale demonstration plant	~ 25,000	probably after 1988

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

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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

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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.

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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 basicresearch 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.

	Identified Research Needs	Site Visit(s)*
1.	Improved designs for pressure let-down values; improved materials of construction for these values.	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 measure- ments, for identification of water-oil inter- faces, 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 with- stand chloride corrosion in vacuum distilla- tion systems and wash columns.	1
9.	Definition of allowable operating variables for sustained controlled dissolver or hydrogena- tion operation.	1,4
10.	Development of quantitative reaction models for component processes; definition of impor- tant 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. Process-research recommendations identified during site visits.

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Table 1.7-1.	(Continued)
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	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 sub- stances containing mineral matter.	2,3
15.	Studies on solvent fractionation and hdyrogena- tion	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.	
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

	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 tech- nique described for the Dow deasphalting units.	6
24.	Careful process costing should be performed for designs using nuclear heat in coal lique- faction.	7

Table 1.7-1. (Continued)

* Legend for Site Visits: 1, SRC Facilities at Ft. Lewis, Washington (May 11, 1979); 2, Gulf Oil Research Laboratory, Harmarville, 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 selec- tivity 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 proc- esses.	1,2
7.	The mechanisms and rates of regressive reac- tions (repolymerizations) occurring during coal liquefaction should be identified.	1,3
8.	Mechanisms and rates of coke formation in pipes should be elucidated.	1,2
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	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 proc- esses should be studied in adequate detail, including quantitative descriptions of the inter- actions 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

Table 1.7-2. (Continued)

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

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The research needs identified by FERWG during site visits are generally consistent with research needs recognized by DOE contrac-Process research needs often refer to urgent practical difficultors. ties 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 <u>Catalytic Effects on the Reactions of Coal in a Donor</u> 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 hydrodenitrification.

(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:

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(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 ZnCl₂);

(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 references 1-25 should be consulted for detailed information; for reviews, see Refs. 1-8.

 $\frac{\text{H-Coal}^9}{\text{-}}$ - 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.

<u>Synthoil</u>¹⁰ - 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.

<u>SRC</u>¹¹ - The iron in the ash is considered to be catalytic. Recycle mineral matter and added iron are being investigated as catalysts.

 $\underline{\text{Dow}}^{12}$ - 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.

 EDS^{13} - 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.

<u>Consol</u>¹⁴ - 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.

<u>University of Utah</u>¹⁶ - 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.

<u>Ruhrkohle/Bergbauforschung</u> - This is a pilot-plant development of a low-pressure version of the Bergius, iron-catalyzed coalliquefaction 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

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2.2.3 Research Needs

Considering only the desired molecular transformations, many of the research needs are identical for coal liquefaction and for coalliquids 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 heteroatom 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.

(h) Identification is needed of a coal-conversion catalyst that is effective at relatively low concentrations (e.g., ~ 100 ppm) and at lower temperatures ($\sim 750-850^{\circ}$ 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 coalliquefaction 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. Pyridineinsoluble 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 solidsseparation 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

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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 (preasphaltenes) 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 donorsolvent 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 petrographicallyidentifiable carbon phases in donor-solvent liquefaction residues.

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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 coalliquefaction 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 semicoke, 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 cokemaking. 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 donorsolvent 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, nondistillable, 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 shutdowns 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 reslurry 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.

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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.

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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 decoking) 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.

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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 $CO-H_2$ 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).

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Licensor	Туре	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 con- struction 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	

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

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.

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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

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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 burnertip 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 coalliquefaction 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 proces 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 Placquemine, 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 designpressure 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

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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 CO₂ 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.



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

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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 subbituminous 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 lowcarbon 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.

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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 vacuumresidue 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.

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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 threestage 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 (~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.

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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 liquefactionand 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.

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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 shearstress 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. 20 11 11

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(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.

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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 rsearch 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.

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(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

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	Jet A	Properties of the 250°F product from severely
Property	specification (ASTM D 1655-78)	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 ⁰ 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. l
end point, ASTM #D86	< 57 2	589
flash point, °F	>100	108

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

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