3.5 RESEARCH NEEDS IN COPROCESSING

3.5.1 Current Research Activities and Status

Coprocessing is the simultaneous liquefaction of coal and the hydrocracking of petroleum resid to produce distillate liquids. The coprocessing technique that will be used at the 11,000-barrel/day plant in Warren, Ohio, is virtually identical to the ebullated-bed technology developed for direct liquefaction.

Coprocessing is a direct outgrowth of direct liquefaction and most of the issues discussed in Section 3.2 apply to this technology as well. Additional complexity is introduced by the chemical dissimilarity between the aromatic coal-derived liquids and the predominantly paraffinic petroleum resid. The effects that this dissimilarity may have on the process have not been studied because of the rapid pace of development to demonstration scale. Certainly, the petroleum resid and its cracked products cannot be expected to have the hydrogen-transfer capabilities of coal-derived liquids, but the effect of this loss of solvent quality has not been investigated. All other aspects of coal-oil interaction, reactivity, and solvating properties must also be investigated.

Other direct liquefaction research areas must be reviewed as well, but with the petroleum reactant/solvent. These research areas include the effects of coal rank and resid composition, catalytic reactivity, and experimental determination of optimum conversion conditions.

Coprocessing is at a state of development similar to that of direct liquefaction ten years ago; demonstration of the technology is being planned with little understanding of the underlying chemistry. In addition, the development program to date has been carried out on a small scale (about 50 pounds of coal per day) so that design and scale-up questions abound. Considerable fundamental research on the coal/oil system and large-scale process development programs are needed to support the demonstration effort. A review of coprocessing is contained in Chapter 7.

3.5.2 High-Priority Recommendations in Coprocessing

This technology will also benefit from most of the research in direct liquefaction. Coprocessing differs from direct liquefaction solely in use of a petroleum reactant/solvent. Accordingly, ten members of the panel recommended a study of the fundamental chemistry of coal/oil reactions. More than one member expressed the opinion that fundamental coprocessing studies are important for learning more about the fundamentals of direct liquefaction. The other high-priority recommendation is to conduct process studies, because optimum reaction conditions are expected to differ from those of direct liquefaction.

3.5.2.1 Study Fundamental Chemistry of Coal/Oil Reactions

The highest-priority recommendation in coprocessing is to study the fundamental chemistry of coal/oil reactions under both catalytic and thermal conditions and elucidate the role of the residuum. In addition, an innovative approach needs to be undertaken to explore new chemical entities to achieve hydrogen donation.

Since coal is a solid hydrocarbonaceous rock, it must be fed to the liquefaction reactor slurried in a solvent. The solvent may either be coal-derived or some other readily available but relatively inexpensive material such as petroleum residuum. When petroleum residuum is used, then coprocessing of coal and residuum occurs with simultaneous upgrading of both materials.

Both coal and petroleum residuum are complex materials composed of many chemical species. Residuum tends to be more aliphatic while coal tends to be more aromatic; however, many different species, particularly compounds containing heteroatoms, are present in both materials. How the residuum and coal interact on a molecular basis is not known. Whether the residuum acts simply as a diluent or as a solvating medium or as a chemical participant in the reactions is open to question.

The objective of this research recommendation is to evaluate and determine the fundamental mechanisms of coal-oil reactions. To understand the chemistry of interaction between residuum and coal compounds, extensive chemical reaction studies need to be performed, using representative model compounds of both coal and petroleum. These reactions need to be carried out under both catalytic and thermal conditions. In addition, incorporation of the actual materials into the reaction systems is also necessary to verify the chemistry. A study of the effect of reaction parameters on these reactions would help to elucidate important parameters in the process chemistry of coprocessing.

The research needs in hydrogen donor fundamental chemistry involve a fundamental chemistry study of how hydrogen donors interact with coal, with petroleum residuum, and with these systems in catalytic environments. In addition, an innovative approach needs to be undertaken to explore new ways and chemical entities to achieve hydrogen donation. This research would involve examining new chemical compound types for hydrogen donability, as well as methods for inducing additional hydrogen donability in coal and petroleum derived solvents.

A thorough understanding of the reaction system involved should provide a sounder basis for process variable choices, catalyst optimization, solvent pretreatment effects, and other process conditions in coprocessing. This fundamental chemistry knowledge base should lead to cost reduction, the amount of which is dependent upon the discoveries made. If a breakthrough discovery is made, the cost reduction in the actual processing of coal and petroleum could be significant.

3.5.2.2 Conduct Process Studies to Determine the Effects of Different Feeds on Reactivity and Product Quality

The second-ranked recommendation in coprocessing is to conduct process studies, including the effects of different feeds on reactivities and product quality. The substitution of a petroleum residuum in place of a coal-derived solvent may result in optimum reaction conditions, catalysts, and coal reactivities that are different from those for direct liquefaction.

Coprocessing is the simultaneous upgrading of both coal and petroleum residuum into higher-value, marketable products. This process has been suggested as the possible first commercialized liquefaction technology to come on stream. Coprocessing relative to direct liquefaction has the advantages of (1) the production of a final product with a chemical composition similar to petroleum but with enhanced octane values due to the aromatics from coal, and (2) the reduction of the metals content of the residuum by deposition on the unconverted coal. Since coprocessing contains more than 50 percent petroleum, materials handling and downstream processing with current petroleum technology are feasible.

Many aspects of the process chemistry of coprocessing need to be evaluated in order to achieve optimal process conditions for thermal and catalytic coprocessing. Some of the process chemistry areas which must be addressed to achieve optimal coprocessing performance are given below. These areas are:

- Determine the influence of residua composition in coprocessing.
- Determine the influence of coal composition in coprocessing.
- Optimize catalysts for coprocessing mixed feeds of coal and petroleum residuum.
- Evaluate the importance and effect of residuum metals on coprocessing.
- Establish criteria for predicting compatibility of coal-petroleum combinations.

- Determine the effect of hydrogen donors and other solvent components on coprocessing.

Research needs in the process chemistry of coprocessing can be summarized as follows:

- Establish criteria for predicting the efficacy and compatibility of different coal-petroleum blends.
- Maximize product selectivity for different coal, petroleum residuum, and catalyst combinations.
- Optimize the catalyst in terms of composition and performance for the mixed feeds in coprocessing.

A thorough understanding of coprocessing process chemistry and optimization of process parameters should yield tremendous benefits for the design of commercial facilities.

3.6 RESEARCH NEEDS IN BIOCONVERSION

3.6.1 Current Research Activities and Status

Bioconversion is currently being tested in three areas of coal processing: to catalyze the CO/H_2 reaction, to desulfurize coal, and to solubilize (liquefy) coal directly. The first two applications have received most of the attention. The anticipated advantages of bioconversion are mild reaction conditions and, possibly, high selectivity to the desired products.

This technology is in its infancy; no process that uses microorganisms to liquefy coal has been demonstrated. At this stage of development, the critical issue is whether bioconversion is a viable method to liquefy coal. Reaction rates are extremely slow and must be improved by orders of magnitude. Of possibly greater concern is that the enzyme system that will liquefy coal may be too costly to produce a product that has only (transportation) fuel value. The cost of nutrients to produce the organism may be greater than the value of fuel products.

Considerable research is needed to develop selective enzyme systems, increase reaction rates, and, probably, develop methods to recover enzymes. Unless these goals are achieved, the application of bioconversion to liquefaction is doubtful. A review of bioconversion is contained in Chapter 8.

3.6.2 High-Priority Recommendation in Bioconversion

The only high-priority recommendation in bioconversion made by the panel is to identify new enzyme systems to facilitate breakdown of coal structure, removal of heteroatoms, and conversion of syngas to alcohol. The panel was in agreement that new enzyme systems that will produce biocatalysts for these selective reactions must be found if bioconversion is to be considered as a potential route to coal liquids.

Bioprocess reactions are catalyzed chemical reactions, except that the catalyst is biologically derived instead of being an inorganic material. Thus, the biocatalyst must have the attributes necessary for a commercially competitive process, high selectivity to the desired products, fast reaction rates, and itself be of reasonable cost. Thus far, no biocatalysts have been found that have all these properties. Reaction rates, especially, must be increased substantially, and the biocatalyst system must be relatively inexpensive to make a product that has transportation fuel value (ca. 5¢/lb).

This research must be performed to determine if bioprocessing has the potential to be an economically viable method to liquefy coal.

3.7 DIRECT CONVERSION OF METHANE

A sixth technology, direct conversion of methane, was introduced during this assessment. The panel heard three presentations about this technology, which converts methane to gasoline directly, without going through the synthesis gas route. Research recommendations were received.

The panel decided that this technology is inappropriate for a liquefaction program. Direct conversion of methane is of interest to industry because of the large reserves of remote gas that would be too costly to transport to markets and, therefore, have no value. Conversion to a liquid (gasoline) would convert this natural gas to a marketable product that could be transported easily. A raw material of no value is thereby converted to a high-valued fuel.

This situation is not pertinent to liquefaction. Current technology developments are minimizing methane production in the gasifier and in the synthesis gas reactor. The methane that is produced certainly is not assigned a value of zero. Therefore, this technology, which affords a great opportunity to produce gasoline via a synthetic fuels route, was not considered in selecting highest-priority research recommendations. The recommendations that were received for direct conversion of methane are shown in Appendix E.

3.8 DOE COAL LIQUEFACTION PROGRAM

In the U.S., because transportation fuels produced from coal liquids are not yet viewed as being commercially attractive, the private sector on its own is not sponsoring a significant amount of research on coal liquefaction. The major sponsor of such research is the U.S. Department of Energy. Over the long term, production of liquid fuels from coal will be required to supplement fuels produced from petroleum supplies.

The first section below presents an overview of the program and its components. The second section discusses the program in Advanced Research and Technology Development, and the third, the program being carried out by the Pittsburgh Energy Technology Center.

3.8.1 Overview

The DOE Coal Liquefaction Program is conducting R&D to develop technologies to convert U.S. coals into fuels that are currently derived from petroleum with an emphasis on producing liquid transportation fuels. The objective of the program is to provide industry with options to produce these clean fuels at lower costs.

The Coal Liquefaction Program consists of long-range applied research on both direct and indirect liquefaction processes. The objective of this research is to provide a technology base that industry can use to achieve coal liquefaction in the most economical and environmentally acceptable fashion when marketplace signals indicate that synthetic liquid fuels from coal are practicable. This research adds directly to the broad understanding of liquefaction, and the results are being used to enhance process efficiency and performance because the effort targets the development of advanced processes. Although commercial technology exists for coal liquefaction (e.g., indirect liquefaction plants in South Africa), economic improvements are essential. Research to date has identified substantial improvements in technology, but additional advances are anticipated through further research to attain the goal of making liquid fuels from coal competitive with those from oil.

The major objectives of the coal liquefaction program are as follows:

- o Develop a data base that industry can use to commercialize coal liquefaction technology when needed.
- o Direct Liquefaction: Develop improved lower-cost process options that provide higher liquid yields and improved product quality at lower capital cost.
- o Indirect Liquefaction: Develop improved technology to product liquid hydrocarbon or alcohol fuels from coal-derived synthesis gas through more efficient, cost-effective processes.

DOE's current coal liquefaction program with research areas is outlined in Figure 3-1. As shown in the figure, the three main program elements are direct liquefaction, indirect liquefaction, and support studies/engineering evaluations. The research areas of interest within each main program element are also shown in the figure.

The objectives of the current program for each research area within each main program element are described further in Figures 3-2, 3-3, and 3-4 for direct liquefaction, indirect liquefaction, and support studies, respectively.

3.8.2 Advanced Research and Technology Development Program

The Advanced Research and Technology Development (AR&TD) Program is a key coal activity within the Office of Fossil Energy (OFE) of DOE. Focused on the fundamental chemistry, physics, and engineering of coal-based processes and on the materials and devices that must be developed to bring such processes to fruition, the AR&TD Program fulfills the needs of basic and applied research within the scope and definition of overall OFE goals. The AR&TD Program is complementary to the line program in coal liquefaction in the OFE. Whereas the line program is oriented toward device and process development, the AR&TD Program is science

Figure 3-1. U.S. Department of Energy Coal Liquefaction Program

The Current Program with Research Areas

Direct Liquefaction

- Advanced Multi-Staged Processing
- Coprocessing
- Novel Concept Research
- Generic Research

Indirect Liquefaction

- Synthesis Gas Conversion to Methanol
- Synthesis Gas Conversion to Liquid Hydrocarbon Fuels
- Synthesis Gas Conversion to Alcohol Fuels
- Light Hydrocarbon Gas Conversion
- Product Upgrading
- Reactor System Hydrodynamics and PCT Properties
- Biological Processing

Support Studies/Engineering Evaluations

- Instruments/Components Research
- Fundamental Research Support
- Liquefaction Technology Data Base

Figure 3-2. **Objectives of the Current DOE Program in Direct Liquefaction**

- o Advanced Multi-Stage Processing
  - Investigate and prove the technical feasibility of advanced multi-stage coal liquefaction concepts having significant potential for state-of-the-art advancements.

- o Coprocessing
  - Evaluate and develop transitional technology having potential for near-term production of coal liquids using, to a large extent, existing petroleum refining facilities and technology.

- o Novel Concept Research
  - Identify and evaluate truly innovative concepts for enhanced direct coal Liquefaction, such as concepts which
    - Operate at substantially lower pressures
    - Operate at low temperatures
    - Reduce or eliminate solvent recycle.

- o Generic Research
  - Perform generic research with potential for widespread applicability to the coal liquefaction technology data base.

Figure 3-3. Objectives of the Current DOE Program in Indirect Liquefaction

- o Synthesis Gas Conversion to Methanol
  - Prove the technical feasibility of liquid-phase technology for methanol production at the PDU scale.
- o Synthesis Gas Conversion to Liquid Hydrocarbon Fuels
  - Identify new or modified catalysts or other innovative approaches which can simultaneously improve conversion activity and suppress adverse yields of wax and light hydrocarbon gases.
- o Synthesis Gas Conversion to Alcohol Fuels
  - Conduct research on innovative homogeneous and/or heterogeneous catalysts for production of ethanol or higher-molecular-weight fuel alcohols at moderate pressures and temperatures.
- o Light Hydrocarbon Gas Conversion
  - Investigate novel approaches for the direct conversion of light paraffinic hydrocarbon gases to alcohol or hydrocarbon liquid fuels.
- o Product Upgrading
  - Evaluate alternative techniques for efficient upgrading of products from conventional and advanced synthesis gas conversion processes.
- o Reactor System Hydrodynamics and PCT Properties
  - Develop a fundamental technical data base on the hydrodynamics of synthesis gas conversion in two- and three-phase systems and on the system characteristics which affect hydrodynamics and transfer properties.
- o Biological Processing
  - Investigate the potential for use of bioorganisms for the selective and efficient conversion of synthesis gas to liquid fuels at mild conditions.

Figure 3-4. Objectives of the Current DOE Program in Support Studies/Engineering Evaluations

o Instruments/Components Research

- Provide adequate instrument and component technology support to the overall liquefaction program through

  = Identifying critical needs/assessing specific deficiencies
  = Developing project requirements
  = Performing research and development
  = Facilitating information availability

o Fundamental Research Support

- Perform fundamental research to enhance understanding of process chemistry, to improve catalyst effectiveness, and to develop guidance for future research.

o Liquefaction Technology Data Base

- Develop a computerized information system whose contents include

  = Liquefaction process data
  = Economic evaluation models
  = Process simulation models
  = Supporting studies
    -- Upgrading data
    -- Pyrolysis assay data
  = Process cost data
  = Feedstock characteristics
  = Bibliographic search capability

oriented, sponsoring fundamental investigations. Project activity in coal liquefaction is focused on fundamental studies where significant efforts are directed to the determination of physical, chemical, and thermodynamic properties; to research in biological coal beneficiation and solubilization; and to the enhancement of catalyst activity/selectivity.

The objectives of the AR&TD coal liquefaction subprogram are to:

- Undertake fundamental studies to improve understanding of coal liquefaction, reactions of synthesis gas, effects of mineral matter in coal, and properties of coal liquids
- Explore new and evolving concepts in coal liquefaction, such as biological conversion and novel catalytic systems that offer the potential for substantially improved performance compared to present systems.

The liquefaction subprogram is based on the generic research needs described above: fundamental studies; novel concepts; physical, chemical, and thermodynamic (PCT) properties; and advanced catalysts. Figure 3-5 identifies specific technical subjects under investigation within each of the primary research areas.

3.8.3 Pittsburgh Energy Technology Center Program

DOE's Pittsburgh Energy Technology Center (PETC) sponsors a significant research program in coal liquefaction and participates in all aspects of DOE's program. The first site visit conducted by the COLIRN expert panel was to PETC to learn the details of PETC's program. The main elements of PETC's program are outlined in Figure 3-6.

Figure 3-5. Research Areas of DOE's Advanced Research and Technology Development Program in Coal Liquefaction

Fundamental Studies	o Reaction Chemistry o Kinetics & Mechanisms o Coal Structure o Sample Bank
Novel Concepts	o Indirect Liquefaction o Biological Approaches o Mild Liquefaction o H_2O-H_2S-CO Chemistry
PCT Properties	o Defined Systems o Undefined Systems o Characterization, Methodology Data Correlation
Advanced Catalysts	o Improved Activity o Improved Selectivity o Anchored Homogeneous o Novel Approaches

Figure 3-6. Pittsburgh Energy Technology Center In-House R&D Program in Coal Liquefaction

DIRECT LIQUEFACTION	INDIRECT LIQUEFACTION	ADVANCED RESEARCH
o Coprocessing	o C_1 chemistry for liquid fuels (oxyhydrochlorination)	o Mechanism of direct coal liquefaction
o Low solvent-to-coal process	o Slurry-phase Fischer-Tropsch catalysis	o Properties of coal, treated coals, and coal slurries
o Catalytic upgrading	o Fischer-Tropsch reactor modeling	o Fundamental studies of coprocessing
		o Bioconversion of coal
		o Structural definition of synthetic fuels
		o C_1 chemistry for liquid fuels (low temperature methanol synthesis)