3.4 RESEARCH NEEDS IN PYROLYSIS

3.4.1 Current Research Activities and Status

Pyrolysis is the thermal low-pressure cleavage and devolatilization of coal to produce gas, liquid, and char. Pyrolysis is carried out at temperatures lower than commercial coking operations in order to maximize recovery of the volatilized product and minimize retrograde reactions that form char. Pyrolysis has always had the appeal of an inexpensive, thermal, low-pressure process that can recover the liquid easily removed from coal. By now, it is evident that the small liquid yield, the low value of the char, and the high cost of upgrading the pyrolysis liquid have prevented commercial application of this technology.

The major product is char. Liquid yields are 0.5-1 barrel per ton; char yield is about 50 percent of the coal. Hydropyrolysis and catalytic hydropyrolysis increase the liquid yield. The major barrier to commercialization is this high yield of char, which has a value (per pound) lower than that of the starting coal. To make this technology economically attractive, liquid yields must be increased substantially.

Some of the comments about direct liquefaction (see Section 3.2) apply as well to pyrolysis, because pyrolysis contains many similar operations. Coal reactivity is influenced by every operation of the process, starting at the mine, and each operation is a suitable topic for investigation. The quality of the pyrolysis liquid requires more attention, because the heteroatom (O,S,N) concentrations are about an order of magnitude higher than in direct liquefaction products, and these impurities are costly to remove. However, the process improvements in these areas are of secondary importance, compared to the overwhelming issue of the low liquid yield.

The development of pyrolysis technology since 1980 parallels the trends of direct liquefaction. Processes that appeared ready for demonstration, including processes developed by FMC, Tosco, Occidental Petroleum, and Rockwell/Cities Service, have been shelved.

In general, pyrolysis processes have the potential to be a less expensive route to coal liquids compared to direct liquefaction because they operate at lower pressure and no hydrogen is needed. In the past, low liquid yields from pyrolysis have been accepted as a consequence of the coal structure and the refractory nature of the aromatic component, but recent findings regarding coal structure have resulted in renewed expectations from pyrolysis. The current picture of coal as consisting primarily of relatively small aromatic clusters with considerable hydrogen bonding indicates that pyrolysis tailored to the coal structure may recover these aromatic clusters as liquid product, rather than as char. It has also been discovered that the highest liquid yield can be obtained under mild pyrolysis temperature (400-800°C) and high heating rate.

A renewed effort in pyrolysis has centered around pretreatment of the coal. This pretreatment changes certain bond energies and allows thermal scission to take place more easily and with greater selectivity than was accomplished by the earlier processes. As a result, liquid yields are being increased dramatically in small-scale tests. These trends may put pyrolysis once again in the position of being an economically viable alternative to direct liquefaction. Although current R&D is at a low level of effort compared to direct and indirect liquefaction R&D efforts, pyrolysis may benefit most from a better understanding of coal and its chemistry. A review of pyrolysis is contained in Chapter 6.

3.4.2 High-Priority Recommendations in Pyrolysis

The recommendation to study the chemistry and the mechanism of catalytic hydropyrolysis had enthusiastic support from eleven panel members because this approach to pyrolysis has the potential to produce high liquid yields, whereas only marginal improvements of thermal pyrolysis processes are anticipated from the other recommendations. The panel believed that large increases in liquid yields are necessary to make pyrolysis competitive with other liquefaction technologies.

The studies of coal structure, reactivity, and devolatilization mechanisms may have beneficial effects if they lead to a new technique that increases liquid yield. Thus, the recommendations in these areas were also given high priority.

3.4.2.1 Study the Chemistry and Mechanisms of Catalytic Hydropyrolysis

The highest-priority recommendation in pyrolysis is to study the chemistry and the mechanisms of catalytic hydropyrolysis.

Recent reports indicate that liquid yields can be increased 2-5 fold over Fischer assay by using a catalytic hydropyrolysis approach. Considerably more detailed information is needed to scope, evaluate, and advance these discoveries. Specifically, variables including catalyst composition and form, temperature, pressure, and residence time must be scoped, and a detailed mechanistic understanding of the chemistry involved must be formulated. Product analysis and evaluation in terms of boiling point distribution, heteroatom content and distribution, aromatic ring distributions, etc., must be determined. A number of coals must be looked at to define the generality of the approach.

A catalytic hydropyrolysis approach which produces >50 percent distillable liquids may be an economically viable alternative to direct liquefaction. The above work is proposed in order to define the potential of this approach. Catalytic hydropyrolysis has been successfully demonstrated at laboratory scale. The development must show that the increased liquid yield and improved product justify the added cost of the hydrogen plant and the high-pressure catalytic reaction system.

3.4.2.2 Characterize Coal Functional Groups and Their Relationship to Pyrolysis/Hydropyrolysis Reactivity

The second recommendation in pyrolysis is to characterize coal functional groups and their relationships to pyrolysis/hydropyrolysis reactivity.

More detailed molecular level coal characterization in terms of functional group distributions is necessary for all coal conversion (to liquids) approaches. Functional groups in this context include heteroatoms (O,S,N) forms and distribution, aromatic ring size distribution, molecular weight between cross-links (physical structure), definition of bridging links in terms of structure and distributions. Correlation of these structural parameters with reactivity -- here defined as pyrolysis and hydropyrolysis -- under different temperature, pressure, and residence time conditions could lead to better understanding of conversion mechanisms.

Better understanding of coal chemical and physical structural parameters and correlation of these with reactivity will provide the knowledge base for further advancements. This is work of a fundamental nature which will provide needed information for the successful development of any pyrolysis process.

3.4.2.3 Study Roles of Reactive Gas in the Devolatization of Coal

The third-ranked recommendation in pyrolysis is to compare pyrolysis yields and products with and without reactive atmospheres (CH_4, CO, CO_2, H_2, H_2O) to understand the roles of these gases in the devolatilization of coal, and seek to understand the chemistry and the mechanisms involved.

Devolatilization rates are the basic information for reactor design and process optimization. There has been little research done on pyrolysis in atmospheres other than inert gases and hydrogen. The use of hydrogen clearly increases the yields of tar and volatiles and results in a better char. Recent work has shown that hydrogen is not the only atmosphere that increases tar yield. Steam, mixtures of steam and hydrogen, and steam and synthesis gas have also been reported to increase tar yields. The results with methane have been contradictory. It is important to continue this research to improve tar yields by developing a better understanding of the effects of operating parameters on devolatilization rates.

This program is easily carried out at a small scale. The results can be gathered and analyzed in a relatively short time period.

3.4.2.4 Conduct Systems Analysis of Pyrolysis/Hydropyrolysis Coupled with Gasification and Combustion

The fourth recommendation in pyrolysis is to conduct a systems analysis of pyrolysis/hydropyrolysis coupled with gasification and combustion.

A major economic limitation to pyrolysis/hydropyrolysis is disposition of the produced char. In general, char is the major product. Use of char as a fuel for combustion or as a feed for gasification could provide an outlet for this product. A systems analysis study is needed to provide guidance as to the potential for coupling a pyrolysis/hydropyrolysis process in front of a combustor or gasifier. Of particular interest is coupling a hydropyrolysis device to an integrated gasification combined-cycle (IGCC) combustion system, where char would be gasified, and the gases scrubbed and then burned. A slip stream of the gases could be used to provide hydrogen for the hydropyrolysis. In hydropyrolysis most of the char would go toward hydrogen production, and the slip stream would be burned for process energy or electricity.

Should a systems analysis show potential, this idea could have immediate impact on the electrical power generation industry. In the most optimistic scenario, liquids produced could be used for peaking cycles or for sale, while the IGCC system would provide higher thermal efficiencies (35-40 percent) versus conventional coal combustion. Most of this work would be an engineering study, based on currently available information.

3.4.2.5 Study Staged Catalytic Hydropyrolysis

The fifth recommendation is to study staged catalytic hydropyrolysis.

Catalytic hydropyrolysis brings to a pyrolysis plant the need for hydrogen production and for high-pressure catalytic reactors. The tar yield is high, but the product quality, as measured by boiling range and heteroatom concentration, is still poor relative to liquids from direct liquefaction. A second catalytic hydrogenation reactor, in which the tar is converted to lighter oils with low heteroatom concentration, would greatly increase the value and utility of the final product, while taking advantage of the availability of hydrogen. Without such a staged approach, it is unlikely that any refinery will be capable of processing the liquid made in a pyrolysis plant. Therefore, this staged approach should be considered for all pyrolysis processes under development.

The results of such a study would enable cost estimates to be done on the use of pyrolysis to make a refinery feed. In scenarios to maximize liquid fuel production, it will be necessary to consider pyrolysis tar (a liquid) as a refinery feed.

This staged approach is a process development, which can easily be added to research on catalytic hydropyrolysis.

3.4.2.6 Study Pyrolysis Reaction Chemistry to Establish Optimum Operating Conditions

The sixth recommendation in pyrolysis is to study the chemistry and the reaction networks in pyrolysis reactions to establish optimum operating conditions.

Much effort in pyrolysis research has been extremely Edisonian. What is needed is more fundamental study on the chemical reactions of coal under the actual reaction conditions used in coal pyrolysis. Conventional model-compound work and work on unrelated polymers are not a part of this recommendation.

It should be possible to establish the pathways for production of methane, ethane, other key hydrocarbons, carbon oxides, hydrogen cyanide, sulfur-containing substances, and so forth.

Thus, it should be possible to relate the changes in process variables with the changes in the product slate to establish the optimum operating conditions. The rate-determining steps can be identified and the opportunities for improvement can be established. This is a fundamental study that is broadly applicable to all pyrolysis process developments.

3.4.2.7 Study Reaction Mechanisms of Steam-Enhanced Pyrolysis

The seventh recommendation is to study the mechanisms of steam-enhanced pyrolysis.

A recent report indicates that steam-enhanced pyrolysis provides 15 percent higher liquid yields compared to conventional pyrolysis, and the liquids are reported to be of higher quality in terms of stability and lower molecular weights. The steam is often introduced under pressure (sometimes at supercritical temperature and pressure). These observations must be quantified and validated. A study is proposed to define the chemistry and mechanism(s). Fluid bed runs must be made to define whether the effects observed are chemical or physical in origin. Products from the system must be segregated by time and analyzed to define boiling point distribution, heteroatom content, etc.

Understanding the mechanism of what is happening could lead to methods of improving further the liquid yields and products. In addition, detailed product characterization could lead to better understanding and improvement of pyrolysis liquid stability.

Steam-enhanced pyrolysis has been tested successfully in laboratory tests. It should be scaled to larger, continuous operations to determine if the results can be duplicated at conditions closer to commercial operation.

3.4.2.8 Study Coal Moisture Effect to Pyrolysis

The last-ranked recommendation in pyrolysis is to study the effects of moisture in coal on pyrolysis and the physicochemical changes that occur during drying or rewetting of coal.

Research on coal structures shows that the inherent moisture may be free water in bituminous coals, but is bound as a gel in lower-rank coals. Drying of these coals results in an irreversible change in structure. Other programs have shown that rewetting under conditions of high temperature and pressure reduces the particle size, exposes new surfaces, and presumably increases reactivity. Thus, drying and rewetting of coals of different rank may have a profound effect on subsequent pyrolysis rates and yields.

This research should be done with the objective of increasing liquid yields with little or no increase in process complexity or cost. The work can be performed at laboratory scale and provide information within a relatively short period of time.

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