CHAPTER 3

COAL LIQUEFACTION R&D RECOMMENDATIONS

3.1 SUMMARY

The twelve-member COLIRN panel assembled for the Assessment of Coal Liquefaction R&D Needs developed and prioritized R&D recommendations in coal liquefaction. The COLIRN panel, with inputs from forty other experts, generated more than 200 ideas, from which 178 research recommendations were developed. These 178 recommendations, which are documented in Appendix E, formed the basis for the panel to screen and prioritize.

Coal liquefaction technologies have undergone significant changes and technical improvements in recent years. These technologies to produce liquid fuels from coal now encompass a number of distinct technologies and processing routes. Because of the diversity of coal liquefaction technologies, the COLIRN panel decided to prioritize R&D recommendations according to six technology categories to prevent domination by any single technology and possible bias. As the result, a comprehensive detailed list of R&D recommendations was generated for each technology, broken down further by general research needs (areas) and by specific research recommendations. The general research needs define areas of an overall research program, while specific recommendations embody specific ideas of work to be carried out. These 178 recommendations were categorized into 57 general research needs (areas) for six technologies under fundamental and applied research.

After reviewing the initial panel evaluations and the high-ranking general research need categories, the COLIRN panel made a final prioritization of detailed specific recommendations at the second panel meeting. This prioritization was accomplished for each technology area by having each panel member choose a small number of recommendations and rank them in order. Points were awarded to the recommendation for each

mention and each position (five for a first place, three for a second, and one for a third, for example). The recommendation garnering the most points was ranked first in that technology area, the next highest total ranked second, and so on.

This methodology yielded thirty-two (32) specific recommendations which were selected to have the highest priority in liquefaction research. These 32 recommendations are listed in Table 3-1 by technology area in order of priority. The table also shows the percentage of the total points (by technology area) won by each recommendation to show the degree of support for that recommendation by the panel. The panel members did not rank specific recommendations in bioliquefaction but rather endorsed the list of recommendations in this area with an indication of the relative importance of the general research needs.

With respect to direct conversion of methane, the panel discussed whether this technology should properly be considered a part of coal liquefaction. The panel's conclusion was that the development of this technology will be driven by resources other than the availability of methane from coal. The recommendations for this technology consequently were not ranked or prioritized.

The high-priority recommendations listed in Table 3-1 are discussed, with supporting information, in the following sections of this chapter. Rationales and opinions by panel members are contained at the end of the chapter, in addition to comments regarding DOE policy and liquefaction programs.

Table 3-1. Summary of High-Priority R&D Recommendations

No.	Description	% of Total Score[*]
Direct Liquefaction		
D1.	Identify structures responsible for retrograde reactions, and determine the mechanism and kinetics of these reactions in order to develop processing strategies that can control them and increase liquid yield. In a broader context, an extensive study is needed of the dissolution and conversion of coal as it is preheated to reactor temperature.	15.8
D2.	Operate a large-scale pilot plant to test engineering and new process concepts, supply samples for other research and upgrading tests, and generate information needed for economic evaluations. The pilot plant must have sufficient flexibility to allow changes in process configuration, operating conditions and feedstocks.	12.0
D3.	Test chemical and low-temperature catalytic pretreatments to enhance coal reactivity, reduce retrograde reactions, or otherwise improve the overall process. These tests must be made in conjunction with the entire process to determine if the cost can be justified by the improvements achieved.	12.0
D4.	Investigate more efficient ways to produce, use, or recover hydrogen.	10.7
D5.	Develop a coal structure - reactivity relationship. Elucidate coal structure features important to liquefaction, e.g., aromatic ring number distribution, "cluster" size, cluster linking groups, population and identity of good hydrogen donors, physical structure, population of bonds capable of thermolysis and cleavage by chain processes, functional group analyses and distribution.	10.1
D6.	Investigate potential homogeneous catalysts for liquefaction. Such catalysts may effect hydrogen addition at significantly lower temperatures, leading to completely new processes.	7.2

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[*]Based on 100% for each technology area

Table 3-1. (Continued)

No.	Description	% of Total Score[*]

Direct Liquefaction

D7.   Develop kinetic models of liquefaction that include   5.9
      the processes of bond breaking, crosslinking, hydrogen
      donation, mass transport, and the effects of solvent.

D8.   Develop chemical techniques to solubilize coal, based   5.9
      on new information of coal chemistry. Major break-
      throughs in processing are likely to require departure
      from high pressure hydrogenation. Many solubilization
      techniques have been developed, particularly for
      analytical purposes, but are uneconomical on a
      commercial scale. Efforts are needed to develop
      economically competitive processes based on such new
      solubilization chemistry.

D9.   Determine the role of mineral matter on initial   5.1
      reactions of coal. This is especially pertinent with
      recent emphasis on deep coal cleaning and "ashy"
      recycle solvent in current process developments.

D10. Develop intrinsic quantitative rate expressions for   5.0
      conversion of individual components and ensembles of
      components as a basis for understanding initial
      reaction paths during coal dissolution.

D11. Develop new catalysts for liquefaction. Current   5.0
      technology has used standard Co-Mo or Ni-Mo supported
      catalysts that seem to perform similarly and require
      substantial thermal severity to perform effectively.
      Unconventional or novel catalysts and supports have
      been considered in fundamental and model compound
      studies. The development of new catalyst systems
      should be related to new liquefaction processing.

D12. Study the mechanism of catalytic hydrogenation and   4.8
      cracking functions to establish their interaction
      and to determine the effects of thermal reaction on
      these functions.

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[*]Based on 100% for each technology area

Table 3-1. (Continued)

No.	Description	% of Total Score*

Indirect Liquefaction

I1.   Apply new advances in materials science to catalyst   22.0
preparation for Fischer-Tropsch and alcohol
synthesis reactions. The preparation techniques may
include production of novel supports, co-
precipitation of catalyst precursors, novel ways of
surface doping, chemical vapor deposition, and plasma
doping. This work should also include new methods of
catalyst characterization by chemical chemisorption,
x-ray diffraction, electron microscopy and
spectroscopies. These new techniques offer major
opportunities for the scientific design of greatly
improved catalysts -- catalysts which would not be
achieved by trial-and-error methods.

I2.   Analyze structure, reactivity, function and role of   21.5
supported organometallic complexes to elucidate the
mechanisms of heterogeneous catalysis in F-T and
alcohol syntheses.

I3.   For the conversion of syngas to alcohols, develop   14.8
routes to maximize ethanol selectivity, minimizing
hydrocarbon yield. Ethanol is already becoming an
important motor fuel or additive.

I4.   Find new catalyzed paths to produce octane-enhancing   13.3
ethers. Ether production may have to be increased
substantially to increase gasoline octane while
reducing auto emissions.

I5.   Investigate maximizing middle distillate yield from   7.1
syngas, with low methane yield. Develop catalysts
for high selectivity to long-chain hydrocarbons that
can be cracked selectively to naphtha and distillate
fuels.

I6.   Develop sulfur-tolerant, low-temperature water-gas   6.6
shift catalysts. Gases made from coal have sulfur
compounds that will be costly to remove to the <ppm
concentration required by current catalysts.

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*Based on 100% for each technology area

Table 3-1. (Continued)

No.	Description	% of Total Score*

Indirect Liquefaction (Continued)

I7.   Study the reaction kinetics and develop alternative   5.1
      catalysts for methanol syntheses to improve process
      economics. New catalysts are needed that have good
      activity with syngas streams but do not require the
      expensive cleanup needed for current catalysts.

I8.   Determine the carbon form that leads to deactivation   4.6
      of F-T catalysts. Define the factors that are
      important in generating the active carbon from CO,
      and the catalyst properties which determine the
      reactivity of this carbon.

I9.   In F-T and related syntheses, use probe molecules to   4.6
      understand and modify product composition. Analyze
      role of poisons and promoters in determining product
      composition. Analyze the possibility of homogeneous
      reactions occurring in F-T.

Pyrolysis

P1.   Study the chemistry and mechanism of catalytic   33.3
      hydropyrolysis. A catalytic hydropyrolysis process
      that produces >50 percent distillable liquids may be
      an economically viable alternative to direct
      liquefaction. Variables, including catalyst
      composition and form, temperature, pressure, and
      residence time must be investigated, and a detailed
      mechanistic understanding of the chemistry involved
      must be formulated. A number of coals must be
      tested to define the generality of this approach.

P2.   Characterize coal functional groups and their   13.9
      relationship to pyrolysis/hydropyrolysis reactivity
      under different temperatures, pressures and residence
      time conditions. Functional groups in this context
      include heteroatom forms and distribution, aromatic
      ring size distribution, molecular weight between
      crosslinks, and definition of bridging links in terms
      of structure and distribution.

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*Based on 100% for each technology area

Table 3-1. (Continued)

No.	Description	% of Total Score[*]

Pyrolysis (Continued)

P3. Compare pyrolysis yields and products with and   13.4
     without reactive atmospheres (CO, CO_2, H_2O, H_2)
     to understand the roles of these gases in the
     devolatilization of coal, and seek to understand
     the chemistry and the mechanisms involved.

P4. Conduct systems analysis of pyrolysis/hydropyrolysis   9.1
     coupled with gasification/combustion to determine
     the technical feasibility and economic incentive for
     char utilization as fuel for combustion or as a
     gasifier feed.

P5. Study staged catalytic hydropyrolysis. The tar made   8.6
     in the first catalytic reaction stage is hydrotreated/
     hydrocracked to reduce heteroatom content and produce
     an acceptable refinery feed.

P6. Study chemistry and reaction networks in pyrolysis   8.1
     reactions to establish optimum operating conditions.
     Perform fundamental studies of the reactions of coal
     under actual pyrolysis conditions in order to
     establish pathways for production of methane, ethane,
     other key hydrocarbons, CO_x, hydrogen cyanide, and
     sulfur compounds.

P7. Define the chemistry and mechanism of steam-enhanced   6.9
     pyrolysis, under both subcritical and supercritical
     conditions for steam. Steam-enhanced pyrolysis may
     lead to increased liquid yields.

P8. Study the effects of moisture in coal on pyrolysis and   6.4
     the physicochemical changes that occur during drying or
     rewetting of coal.

Coprocessing

C1. Study the fundamental chemistry of coal/oil reactions   51.6
     under both catalytic and thermal conditions. Elucidate
     the role of the residuum. In addition, an innovative
     approach needs to be undertaken to explore new chemical
     entities to achieve hydrogen donation.

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[*]Based on 100% for each technology area

3-7

Table 3-1 (Continued)

No.	Description	% of Total Score*

Coprocessing (Continued)

C2.   Conduct process studies in coprocessing, including   17.2
        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 than for
        direct liquefaction, and these conditions must be
        determined.

Bioliquefaction

B1.   Look for new enzyme systems that will produce new   76.9
        biocatalysts for specific reactions to facilitate
        the breakdown of the coal structure, removal of
        heteroatoms, or conversion of syngas to alcohols.

*Based on 100% for each technology area

3.2 RESEARCH NEEDS OF DIRECT LIQUEFACTION

3.2.1 Current Research Activities and Status

Direct liquefaction is the reaction of coal with hydrogen. The coal is slurried in a process-derived solvent that transfers or shuttles hydrogen to the coal or coal liquids. The reaction is usually carried out at high pressure.

The evolutionary changes that have occurred since 1980 have been the overall shifting of coal liquefaction development from high-severity single-stage processes to low-severity two-stage processes. Consequently, the emerging direct liquefaction R&D activities now focus on:

o   development of integrated two-stage liquefaction processes

o   investigation of direct liquefaction coprocessing variables and catalyst optimization

o   development of novel catalysts

o   refining and upgrading of coal liquids to marketable transportation fuels.

The changes in processing that have emphasized less severe liquefaction conditions have resulted in greater liquid yield and more efficient hydrogen utilization. Other major advances that have taken place in solid-liquid separation (deashing) and catalyst development have contributed to the greater liquid yield and improved product quality that have contributed to significantly improved process economics.

Currently, the most important direct liquefaction process is Catalytic Two-Stage Liquefaction (CTSL), in which coal is liquefied in a catalytic ebullated-bed first stage reactor and the coal liquids are subsequently hydrotreated/hydrocracked to distillable liquids in a second-stage reactor of similar design. The liquids are suitable for upgrading to transportation fuels by conventional refinery operations.

The solvent, including resid, is recycled from the second stage. Mineral matter is removed after the second stage. CTSL is under development at the two largest direct liquefaction units under contract to DOE -- the 6-tons/day PDU at Wilsonville, Alabama, and a 50-pounds/day bench unit in Trenton, New Jersey.

This technology requires a large hydrogen consumption to increase the H/C atomic ratio from 0.8 in the coal to 1.7-2.0 in the finished products, transportation fuels. The cost and the efficient use of hydrogen have, therefore, always been major concerns. Another concern is the costly high-pressure hydrogenation reactors. Developments in the 1980's have resulted in somewhat less severe reaction conditions, but the system pressures of about 3000 psig, reaction temperatures of about 800°F, and use of back-mixed reactors result in costly process equipment. Research that leads to more efficient hydrogen usage, a more active catalytic system, or less costly processing will improve direct liquefaction economics significantly.

At the same time, fundamental research has yielded new understanding of coal structure and chemistry, hydrogen transfer liquefaction mechanisms, and product characterization. However, this new understanding of liquefaction has not as yet been incorporated into process developments, which are basically extensions and improvements of the processes of the 1970's.

The prevailing current understanding, based on laboratory tests, is that coal liquefies more easily than had previously been thought, but the liquefaction products also re-combine rapidly. These "retrograde" reactions, which may begin while the coal is being heated to reaction temperature, produce molecules that are more refractory than the original coal and require the current severe reaction conditions to cleave the molecules and produce liquids. If these retrograde reactions can be avoided, it should be possible to liquefy coal directly to distillable liquids in a single stage, and at much milder conditions than heretofore utilized successfully. These new concepts about retrograde reactions

3-10

have not as yet been developed and tested as part of a liquefaction process.

Other issues exist for a technology that actually starts at the coal mine mouth. A critical issue continues to be the reactivity of the coal, and maintenance of its reactivity through all stages of coal preparation and preheating. Coal rank is also a major variable of reactivity, and it may be advantageous to develop more than one process, each designed to be the most efficient for a particular coal rank. There may be justification to deep-clean the coal to low mineral-matter concentrations to simplify processing and reduce corrosion/erosion. The current deashing techniques were developed to recover non-distillable boiler fuels; they may not be suitable to current processes and products. Therefore, the very important issue of mineral-matter removal, either upstream of the process or after liquefaction, may require a new approach.

In the investigations of one or more of these issues, the impact on the entire process must be considered. Few, if any, of the issues can be addressed effectively in isolation of the entire liquefaction process.

3.2.2   High-Priority Recommendations in Direct Liquefaction

Direct liquefaction technology has several steps, each of which can be improved by further research. These steps include preparation, preconversion chemistry, liquefaction and upgrading, mineral-matter removal, solvent preparation, and product refining. As a result, there was no one area of research that dominated the selection of highest-priority recommendations. No research recommendation received the support of more than seven panel members, and a total of 12 received support from at least two. Of the first five highest-priority recommendations in Table 3-1, two (Nos. D1 and D3) are directed to investigations of coal reactions before the first reactor, and another (No. D5) is to develop a coal structure-reactivity model. The second recommendation (No.D2) is to operate a large-scale unit so that the U.S.

3-11

will continue to have the capability to obtain information for the design of demonstration-scale units. Clearly, however, most of the recommendations favor fundamental research, possibly leading to new processes, rather than support of current processes under development.

The study of coal structure was recommended by the panel twice-- once in the direct liquefaction program and again in pyrolysis. Although this may be redundant, it is understood that the investigators in the two technologies may be interested in different aspects of coal structure.

One high-priority recommendation (No. D4) is for a general research need -- investigate more efficient ways to produce, use, or recover hydrogen -- rather than for a specific research recommendation. Hydrogen usage is a major element in process economics, but no outstanding research recommendations in this category were received.

3.2.2.1 Identify Coal Structures Responsible for Retrograde Reactions and Determine Their Mechanisms and Kinetics.

The highest-priority recommendation in direct liquefaction is to identify structures responsible for retrograde reactions and determine the mechanisms and kinetics of these reactions in order to develop process strategies to control them and increase liquid yield.

During coal liquefaction, the break-up of the coal macromolecular network is controlled by the relative rates of bond breaking, crosslinking (retrograde reactions), and mass transport. High rates of crosslinking lead to a small amount of low-molecular-weight liquids and a large insoluble fraction. Crosslinking, as measured by solvent swelling experiments, is observed to be rank dependent, with lignites crosslinking at lower temperatures than bituminous coals. Crosslinking has a major impact on the yield and molecular weight distribution of coal liquids. In addition, the molecular weight distribution of the liquid products has a major effect on the efficiency of utilization of the coal's hydrogen. The study of crosslinking and how to control it can have a major impact on improved liquefaction processes.

3-12

A program should be pursued to develop techniques to characterize crosslinking and to determine the mechanisms of its occurrence, rate, and dependence on coal rank. With this information methods should be pursued to control crosslinking to optimize liquefaction yields and product quality. If successful, this work should lead to less severe liquefaction conditions, which translates into lower capital and operating costs.

The current work on coal chemistry and reactivity has great potential to generate much needed information. Results should be available within a few years and, combined with a model of coal structure, will provide a fundamental basis for development of liquefaction processes.

3.2.2.2 Operate a Large-Scale Pilot Plant to Test Engineering and New Process Concepts

The second-ranked recommendation in direct liquefaction is to operate a large pilot plant to generate the information needed to scaleup to commercial- or demonstration-scale operation. Small bench-scale units are used for investigating liquefaction chemistry. Small PDUs of 50-200 lb/day capacity then are used to test process concepts on a continuous-flow, integrated basis. The next useful size is that of Wilsonville (3-6 tons per day). This size allows the use of commercial-type equipment to prove the chemistry, provide proof of concept of the process under development, and generate enough information for conceptual process design and economics. It also is needed to maintain technical readiness for demonstration.

There is an unfulfilled need for the next-sized plant, one with a capacity of about 200 tons/day. The U.S. coal liquefaction program has benefited enormously from the information gathered at Catlettsburg (H-Coal), Fort Lewis (SRC-II), and Baytown (EDS) pilot plants in the past, even though the processes did not prove to be economically attractive at the time. The Germans have had an ongoing program at Bottrop for years,

and the Japanese are committed to two long-term, large-scale pilot plants -- a 150-ton/day bituminous coal plant and a 50-ton/day brown coal plant in Australia. The U.S. needs such a facility to remain competitive.

3.2.2.3   Test Chemical and Low-Temperature Catalytic Coal Pretreatment

The third recommendation in direct liquefaction is to test chemical and low-temperature pretreatments to enhance coal reactivity, reduce retrograde reactions, or otherwise improve the overall process. A variety of chemical technologies have been proposed or tested in laboratory programs. These need to be tested in conjunction with the rest of the conversion processes to see if their costs can be justified by the improvements offered.

The catalytic reaction of coals at sub-pyrolysis temperatures appears to invoke structural changes that can determine the course of subsequent reactions at (possibly) higher temperatures. This is the basis for staged catalytic liquefaction, which can lead to higher selectivities to desirable products.

It has yet to be established how staged liquefaction influences the quality of the products and the ease with which they can be further upgraded. Of equal importance are the basic changes in coal structure that are caused by low-temperature catalytic reaction. In some cases, these are subtle and not easily detected by conventional analyses. There is a need to quantify and interpret these changes.

3.2.2.4   Investigate More Efficient Ways to Produce, Use and Recover Hydrogen

The fourth recommendation in direct liquefaction is to investigate more efficient ways to produce, use, or recover hydrogen.

Hydrogen production is a major cost of a direct liquefaction plant. With the current CTSL processes making more liquid with a higher H/C ratio, hydrogen consumption is increased. The cost of coal liquids would

be reduced considerably if hydrogen were to be produced at lower cost or if hydrogen use were reduced (by making less hydrocarbon gases).

This is a high-risk research program. Cheaper ways to make hydrogen have been the goal of several investigations over many years, with no success. Hydrocarbon gas yields have been reduced by almost 50 percent in the last few years, but further decreases will be difficult. Nevertheless, the potential improvement in liquefaction economics is so great that novel approaches should be sought and supported.

3.2.2.5   Develop a Coal Structure-Reactivity Model

The fifth recommendation in direct liquefaction is to develop a coal structure-reactivity model. Elucidate coal structure features important to liquefaction chemistry; examples include, but are not limited to, aromatic ring number distribution, "cluster" size, cluster linking groups, population and identity of good hydrogen donors; physical structure, population of bonds capable of thermolysis and cleavage by chain processes, functional group analysis and distribution.

The reactivity of coal in various conversion processes is known to be dependent on coal rank. While this variability in reactivity has been attacked in a statistical manner, the fundamental structures responsible for controlling and/or limiting coal reactivity are not known. Identifying such limiting features is a necessary first step in rational attempts to achieve the maximum possible coal reactivity. Characterization of reactive structures would make it possible to select the best coals for given processes based on inexpensive determinations of coal structure rather than highly expensive pilot plant studies. It may also be possible to determine the variation in coal reactivity over the large coal reserves required to feed commercial conversion plants. This coal structure-reactivity correlation will prove extremely useful in future process developments.

3.2.2.6 <u>Investigate Potential Homogeneous Catalysts for Direct Liquefaction</u>

The sixth recommendation in direct liquefaction is to investigate homogeneous catalysts for direct liquefaction. Homogenous transition metal complexes, such as metal carbonyls, give finely dispersed metal oxide or sulfide catalyst particles at high temperatures. In addition, such catalysts selectively add H_2 to coal at mild conditions ($\sim 200^{\circ}C$). These catalysts have exhibited good activity in coprocessing.

Work is needed to determine the state of the catalyst during and after reaction, and its dispersion in direct liquefaction and coprocessing. This research is an excellent opportunity to study dispersion and chemical (as well as physical) forms of the catalyst during direct coal liquefaction and in coprocessing.

From a fundamental point of view, this work may lead to a better understanding of the mechanisms of catalyzed reactions and hence to novel catalytic processes.

3.2.2.7 <u>Develop Kinetic Models of Direct Liquefaction</u>

The seventh recommendation in direct liquefaction is to develop kinetic models of direct liquefaction. Several models, which have significant potential in modeling coal liquefaction, have recently been developed to describe the thermal decomposition of coal. These new models consider the processes of bond breaking, crosslinking, hydrogen donation, and mass transport by a statistical treatment of a lattice which represents the coal macromolecule. Such models can provide a basis for understanding and testing the chemistry and mass transport mechanisms in coal liquefaction.

A program should be pursued to adapt these models to liquefaction conditions by incorporating the added effects of the solvent. The models should be expanded to include the chemistry of liquefaction in more detail and test this proposed chemistry by comparison to liquefaction

3-16

data. It is believed that better understanding of the competitive roles of bond breaking, crosslinking, hydrogen donation, mass transport and solvent effects can lead to new and improved liquefaction technologies.

Although fundamental in nature, the incorporation of solvent effects into the model will provide information related to optimum solvent properties. Process conditions will undoubtedly need to be modified to change solvent properties. Therefore, this work could have a significant impact on process developments.

3.2.2.8 Develop New Chemical Techniques to Solubilize Coal

The eighth recommendation in direct liquefaction is to develop new approaches to break down and solubilize coal into liquids using chemical techniques.

Current technology has improved but not changed basic liquefaction chemistry that originated in Germany over fifty years ago. Major breakthroughs in processing are likely to require new chemistry. Many techniques have been developed for analytical purposes, particularly for studying coal structures, that are uneconomical. Effort is needed to see if processes can be derived, building on new information being developed in coal chemistry. For example, almost complete conversion of coal can be achieved by alkylation with methanol. The improvement over earlier alkylation research is that very low quantities of methanol are needed to achieve this result. Other laboratories are using strongly acidic reactants.

This is a high-risk program, because chemical methods of liquefaction require expensive starting materials. The process may be uneconomical unless the chemical usage is low or the reactant can be recovered cheaply. Also, many acidic systems are corrosive, requiring expensive materials of construction. However, such approaches must be considered as a way to liquefy coal without having to use high-pressure hydrogenation.

3.2.2.9 Determine the Role of Mineral Matter on Initial Solubilizing Reactions of Coal

The ninth recommendation in direct liquefaction is to determine the role of mineral matter on initial dissolution reactions of coal.

There is some evidence that the rate of retrograde reactions may be related to the inorganic constituents in the coal. Observations have been made that some demineralized coals produce higher levels of tar in pyrolysis and more fluid chars in combustion. Both of these changes are consistent with lower rates of crosslinking. A study should be undertaken to determine the relationship between crosslinking and the inorganic constituents in coal. With this information methods should be pursued to control retrograde reactions to optimize liquefaction yields and product quality.

This work is especially pertinent at this time because of the interest in deep cleaning, which will reduce mineral matter to concentrations far lower than used heretofore. On the other hand, the use of "ashy" recycle in current process schemes concentrates the mineral matter by a factor of 2-3 over the concentration in the coal slurry feed to the reactor. The proposed program will provide insight as to the benefits, if any, to liquefaction that are provided by the mineral matter.

3.2.2.10 Develop Intrinsic Rate Expressions for Initial Coal Dissolution Reactions

The tenth recommendation in direct liquefaction is to develop intrinsic rate expressions for conversion of individual components and ensembles of components as a basis for understanding initial reaction paths during coal dissolution. This work is not intended to lead to a new process, but will generate an understanding of the basic chemical fundamentals underlying liquefaction and provide predictive capabilities to optimize liquefaction processes generally.

3.2.2.11 Investigate Unconventional Catalyst Systems for Direct Liquefaction

The eleventh recommendation in direct liquefaction is to investigate unconventional catalyst systems.

Conventional supported catalysts have been extensively investigated in direct coal liquefaction. In very general terms these seem to perform similarly, rapidly losing a high initial activity, and requiring substantial thermal severity to function effectively. A number of sequential catalytic treatments are needed to produce finished products.

Unconventional catalysts and supports have been considered in fundamental and model studies, and some, such as molten $ZnCl_2$, have been used at fairly large scale. However, there has not been a great deal of work done to bring these unconventional systems to the point at which speculative processes can be designed and evaluated. A major deficiency is the lack of work with coal to produce something like finished products.

This is a highly speculative venture; successful results cannot be forecast. However, in spite of the high risk, the potential impact could be large, since an unconventional catalytic process could radically alter the current concept of a coal liquefaction process. Some breakthrough in this area could also significantly impact processes for heavy oil upgrading.

3.2.2.12 Study the Mechanisms of Catalytic Hydrogenation and Cracking Reactions

The last recommendation in direct liquefaction is to study the mechanisms of catalytic hydrogenation and cracking functions to establish their interaction and to determine the effects of thermal reactions on these functions.

Conversion of coal to liquids requires several reactions -- bond breakage, hydrogenation, conversion (cracking) of the coal resid to smaller molecules, heteroatom removal, and hydrogenation of the liquid

product.   These reactions require both catalytic cracking and hydrogenation functions.   In addition, thermal cracking probably plays a key role, especially in coprocessing, where the paraffin petroleum resid undergoes extensive thermal cracking at reaction temperatures.

If the mechanism of each of these reactions is understood and quantified, reaction conditions could be selected to maximize the yield of high-quality liquid products.   This work is of a fundamental nature, and the results would support the development of any direct liquefaction or coprocessing process.

3.3 RESEARCH NEEDS OF INDIRECT LIQUEFACTION

3.3.1 Current Research Activities and Status

Indirect liquefaction involves the gasification of coal to synthesis gas ($CO + H_2$) and the subsequent conversion of the syngas to fuels and chemicals. The process involves breaking every bond in the coal structure. The subsequent conversion of the syngas involves the use of a catalyst in every case. Methane is the most thermodynamically favored product and methanol among the least favorable. Syngas is being converted to methane at the Great Plains Gasification Plant. At present, methane is not a product of critical need, since natural gas is available.

Commercialized indirect liquefaction processes include the following:

o   The Fischer-Tropsch (F-T) Process. This is practiced commercially only in South Africa. The SASOL F-T processes convert almost 70,000 tons of coal per day to syngas. The gas is then converted over a cheap iron catalyst to 86,000 barrels per day of gasoline, diesel fuel, ethylene, ammonia, sulfur and other products. The process involves a polymerization of $-CH_2-$ units and, unfortunately, yields a melange of products, from methane to high-molecular-weight materials. There is now much interest in using syngas with low H_2/CO ratios from modern coal gasifiers for conversion to wax for cracking to desirable distillates; little methane is formed under these conditions.

o   Methanol from Syngas. Methanol is one of the ten largest-volume organic chemicals, produced worldwide at an annual rate of over three billion kg. It is made in numerous plants in greater than 99 percent selectivity when a mixture of CO, H_2, and CO_2 is passed over a $Cu/ZnO/Al_2O_3$ catalyst at about $250^\circ C$ and elevated pressures. Methanol has a high octane number and can be used as a fuel for internal combustion engines. Blends of methanol with cosolvent alcohols are used in varying amounts as octane-enhancing additives in gasoline. Methanol is also a small part of methyl tertiary-butyl ether (MTBE), which is an excellent octane enhancer in gasoline. A liquid-phase methanol process is being developed by Air Products at their 10-tons/day PDU in LaPorte, Texas. The process uses a H_2/CO ratio of 0.8, which is typical of syngas made from coal.

o   The Mobil (MTG) Process. In this process, practiced on a large
     scale in New Zealand, syngas is converted to methanol, which is
     then passed over a shape-selective catalyst (ZSM-5) to yield
     92-93 octane gasoline. New Zealand selected the MTG process
     over the F-T process because the former was much more
     selective, involved fewer upgrading steps, and involved simpler
     engineering. Some 14,000 barrels per day of high-octane
     gasoline is now being produced in New Zealand using the MTG
     process. At the present price of petroleum, this plant is
     uneconomic.

Many innovative and important research and development efforts to
improve indirect liquefaction technology have continued during the
1980's. The major thrust of these new research efforts includes the
following:

o   Direct synthesis and optimization to produce higher-alcohol
     fuels from syngas. Work in this area includes the development
     of a homogenous catalyst, and binary and ternary heterogenous
     catalysts.

o   Optimization of the process variables and the catalyst to
     obtain a product that can be upgraded by conventional
     hydrocracking techniques to produce diesel and gasoline-range
     hydrocarbons.

o   Modification of the Fischer-Tropsch catalyst to limit the
     conventional chain growth mechanism governed by the Shulz-Flory
     distribution. This includes the use of size- and shape-
     selective zeolite catalysts, the development of promoted
     catalysts with alkali, and the operation of the catalytic
     reactor systems at lower temperatures.

o   Development of a slurry-phase Fischer-Tropsch catalyst and
     reactor system that can synthesize hydrocarbons from the
     hydrogen-lean synthesis gas ($H_2/CO<1.0$) produced from the new-
     generation gasifiers.

The potential of these emerging indirect liquefaction technologies
is recognized, and a number of research and development activities are
already underway. Table 3-2 summarizes the representative R&D activities
that are currently being pursued by both government and private industry.
These activities and other current research are described in more detail
in Chapter 5, which contains a review of indirect liquefaction.

Table 3-2. Emerging Indirect Liquefaction R&D Activities

Major Research Area	Representative R&D Activities
Direct synthesis of higher alcohols	- Search for novel homogeneous catalyst - Modify ruthenium catalyst - Develop binary Cu/ZnO catalyst and Cu/ZnO/Al$_2$O$_3$
Fischer-Tropsch process variables and catalyst optimization	- Understand wax formation from F-T process variables - Study mechanism of F-T catalysts - Novel catalyst for the selective synthesis of gasoline and diesel - Suppression of CH$_4$ formation in F-T synthesis - Surface properties of F-T catalysts - Promoted catalyst development
Limitation to F-T chain growth	- Novel carbon molecular sieve catalyst for wax suppression - Multifunctional catalyst for direct liquid fuel synthesis - MTG ZSM-5 catalyst to produce gasoline from methanol
Slurry-phase catalyst and reactor system	- Develop slurry-phase F-T catalyst - Hydrodynamics of F-T synthesis in slurry bubble column reactor - Diffusibility and solubility of syngas and F-T products in slurry media
Biological technology to produce liquid fuels from coal	- Biological conversion of coal derived synthesis gas to liquid hydrocarbons - Design and select microorganisms to achieve desired biochemical activity

3.3.2 High-Priority Recommendations in Indirect Liquefaction

This technology has fewer areas for research because it starts with CO/H_2 instead of coal and the products are either hydrocarbons similar to petroleum streams or oxygenates that need no further processing. Consequently, the research recommendations were concentrated on the synthesis reaction itself -- catalysts, control of product distribution, or reactor configuration. The first two recommendations (Table 3-1), which apply to all CO/H_2 reactions, were supported by at least nine panel members; the other seven recommendations were selected by 2-6 panel members.

Although the recommendations are fairly well balanced between Fischer-Tropsch and oxygenate synthesis, the panel felt that the major interest in indirect liquefaction will be to produce alcohols and ethers as fuels and octane enhancers.

3.3.2.1 Apply New Advances in Materials Science to Catalyst Preparation for F-T and Alcohol Synthesis

The highest-priority recommendation in indirect liquefaction is to apply new advances in material science to catalyst preparation for Fischer-Tropsch and alcohol synthesis reactions.

It is desirable to apply to the catalyst field the major advances in materials science made by high-technology science and industry. Thin layers, monolayers and sub-monolayers of dopants are well controllable today, both by modern preparation methods and by modern characterization tasks. Whereas Europe has annual conferences to review the extensive research in materials science of catalysts, no concerted U.S. effort exists except for single crystal surface science. This work should include research on novel supports, co-precipitated catalyst precursors, novel ways of surface doping, chemical vapor deposition, and plasma doping. Catalyst characterization techniques should included specific chemisorption, x-ray diffraction, electron microscopy, and other spectroscopic techniques.

This research is long range and may possibly result in no significant improvements in indirect liquefaction. The possibility, however, does exist that a completely new catalyst may be discovered that could greatly improve process economics.

3.3.2.2 Analyze the Structure, Reactivity, Function, and Role of Supported Organometallic Complexes

The second-ranking recommendation is to analyze the structure, reactivity, function, and role of supported organometallic complexes to elucidate the mechanisms of heterogenous catalysis in Fischer-Tropsch and alcohol synthesis.

Improved understanding of reaction sequences provides an ideal route for improvement of catalytic processes. Many highly dispersed catalyst systems form surface compounds that are, or resemble, organometallic complexes. Thus, a preferred route to advance understanding in this area is to add organometallic or other cluster complexes to a suitable catalyst support. Studies should then be conducted to elucidate the changes these complexes undergo in attaining reaction conditions which will define the nature of the active site in the working catalyst. Emphasis should be placed upon studies that will utilize these organometallic complexes in reactions, both chemical and catalytic, to elucidate the mechanisms of catalytic reactions and the features imparted by the support.

3.3.2.3 Develop Catalytic Conversion Routes to Maximize Selectivity of the Conversion of Synthesis Gas to Ethanol

The third-ranking recommendation is for the conversion of syngas to alcohols, to develop routes to maximize ethanol selectivity.

Ethanol is a proven transportation fuel, used straight as well as blended in hydrocarbon fuels. It has advantages compared to methanol- it is relatively non-toxic, blends better with hydrocarbons, does not absorb as much water, and is relatively non-corrosive. Yet, ethanol has

a high octane number (BON 110, MON 92, RON 96), low emissions, and has been mandated in Colorado and Nebraska, and sold in other states. An improved process starting with syngas will probably be cheaper than the fermentation route.

This research has a high probability of success, and results could be forthcoming in a relatively short period of time.

3.3.2.4 Find New Catalyzed Paths to Produce Octane-Enhancing Ethers from Alcohols

The fourth recommendation is to find new catalyzed paths to produce octane-enhancing ethers from alcohols.

Ethers, as octane enhancers, are becoming a significant component of transportation fuels. As such, they may make up to 10 percent of the gasoline volume. Even for the currently used methyl tertiary-butyl ether (MTBE), the synthesis route is dictated by an economical source of both methanol and isobutane. With increasing demand other ethers utilizing other raw materials will become a necessity. Even in the case of MTBE, which is a commercially accepted and heavily used octane enhancer, new raw materials, catalysts, and reaction pathways may be required to satisfy growing demand. Thus, exploratory research is needed to define a group of catalytic materials that will provide a basis to utilize a range of potential feedstocks for ether production. Production can then change to follow market supply and price of potential feedstocks.

3.3.2.5 Investigate Catalysts to Maximize Middle Distillate Yield from Syngas

The fifth recommendation is to investigate maximizing middle distillate yield from syngas, with low methane yield. Develop catalysts for high selectivity to long-chain hydrocarbons which can be cracked selectively to naphtha and distillate fuels.

The Fischer-Tropsch reaction can be controlled to produce a high yield of long-chain hydrocarbon middle distillates and waxes, which can

3-26

subsequently be cracked to naphtha and lighter distillate precursors of gasoline, jet fuel, and diesel fuel. Driving the reaction of these products will minimize production of methane. The catalyst must have high selectivity for the production of long-chain hydrocarbons. Additional catalyst development will be needed to obtain selective cracking of the wax. This route to transportation fuels may be more economical than other coal conversion processes.

This research has an excellent chance for success in a relatively short time.

Shell has announced work in this area, but has not published results. UOP is developing a wax hydrocracking process.

3.3.2.6 Develop Sulfur-Tolerant Low-Temperature Water Gas Shift Catalysts

The sixth recommendation in indirect liquefaction is to develop sulfur-tolerant low-temperature water gas shift catalysts.

The current low-temperature (below $250^{\circ}C$) water gas shift (WGS) technology utilizes copper-based catalysts, which are extremely sensitive to sulfur (<= lppm) and chloride (<= 0.1 ppm) poisoning. The element having such sensitivity is the copper. To avoid an extremely demanding cleanup of the water gas (CO + H_2O+ impurities), it is desirable to develop a catalyst and a process for WGS that works at temperatures below $250^{\circ}C$ equally well as the copper catalysts but is insensitive to sulfur and chlorine. A class of catalysts that may satisfy these conditions is transition metal sulfides promoted with alkali.

3.3.2.7 Study the Reaction Kinetics and Develop Alternative Methanol Synthesis Catalysts

The seventh recommendation in indirect liquefaction is to study the reaction kinetics of, and develop alternative catalysts for, methanol synthesis to improve process economics.

Methanol continues to become more attractive as a transportation fuel, from both economic and environmental viewpoints. Today, some regions of the U.S. appear ready to mandate the use of methanol as a gasoline substitute. With increased demand it becomes imperative that the development of improved or alternative methanol synthesis catalysts be emphasized and accelerated. An effort is required to develop catalysts having improved performance with current-quality synthesis gas streams. However, catalyst research should strive especially to develop catalysts that do not require the extensive and expensive cleanup required by current catalysts. Additionally, catalysts should be sought that have the capacity to operate in reactors having unique capability to handle the heat of reaction for this exothermic reaction.

3.3.2.8 Determine the Carbon Form that Leads to Deactivation of F-T Catalysts

The eighth recommendation in indirect liquefaction is to determine the carbon form that leads to deactivation of Fischer-Tropsch catalyst.

In recent years, application of numerous surface science characterization techniques has identified a carbon surface species as an active intermediate associated with syngas conversion. The chemical nature of this species should impact the selectivity for Fischer-Tropsch synthesis. A number of factors could potentially determine the chemical character of this carbon species; these include catalyst promoters, catalytic metal, presence of other adsorbed gases, etc. A coordinated effort should be directed toward defining the factors which are important in generating the active carbon from carbon monoxide, and the catalyst properties which determine the reactivity of this carbon. These efforts should include work directed toward the actual high-pressure conditions encountered with a working commercial catalyst.

3.3.2.9 Use Probe Molecules to Study Product Composition in F-T and Related Synthesis

The last-ranked recommendation is to use probe molecules to understand and modify product composition in Fischer-Tropsch and related syntheses.

3-28

The Fischer-Tropsch synthesis of hydrocarbons from synthesis gas has been, apart from a brief period of methanol-to-gasoline synthesis in New Zealand, the only commercial-scale synfuels process in operation during the past ten years. It must therefore remain an important alternative in any energy policy. In spite of the extensive research already carried out and the inability, to date, to alter the product distribution from that required by the Anderson-Schulz-Flory polymerization scheme, additional research in this area would be valuable.

Three research areas to generate fundamental mechanistic understanding should be emphasized. First, the use of probe molecules, appropriately labeled by an isotope or other identifiable chemical characteristic, to better understand the nature of the surface species and to understand the mechanistic implications is essential. Second, in commercial operation it is an exceptional case when a catalyst is used without modification by a promoter, such as potassium in the Fischer-Tropsch synthesis, or an appropriate poison, such as sulfur in commercial Pt-Ru reforming catalysts. Fundamental studies should be directed toward understanding how promoters and poisons alter catalytic properties for commercial iron-based F-T catalysts as well as for novel catalyst materials. Third, the Fischer-Tropsch synthesis is one of the few instances where there are many homogeneous cluster catalysts which effect syngas conversion, and these should be effectively utilized to develop detailed mechanistic understanding of the synthesis. This appears to be a unique opportunity to build an understanding and bridge the gap between well-understood homogeneous catalytic reaction mechanisms and those of the much more complex, but much more practical, heterogeneous catalysts.